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PART C
LIQUID & SOLID WASTE RESEARCH

Organized by
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Corporate Resources Division
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Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

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The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:

Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
Part E: Environmental Economics.

This part is a collation of those papers presented at Session C of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

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HAZARDOUS WASTE THERMAL DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS

By

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ABSTRACT

Since 1980, the U.S. Environmental Protection Agency (EPA) has conducted extensive research to assess the performance of hazardous waste thermal destruction processes. This research has been designed to support the development and implementation of regulations and standards for controlling the safe operation of thermal destruction facilities in the United States. While these studies have largely shown thermal destruction to be the most practical and effective technology available for ultimate control of organic hazardous waste materials, some members of the scientific and environmental action community remain concerned about the long-term safety of the technology. The issues most frequently raised pertain to the possibility that harmful levels of heavy metals and incomplete combustion by-products may still be emitted from thermal destruction facilities that are otherwise meeting the current RCRA standards. The lack of available real-time monitoring techniques for tracking thermal destruction efficiency and detecting possible process upsets adds to the uncertainty and perceived risks associated with facility operation.

This paper will summarize the most recent data on thermal destruction facility performance with particular attention to metal and organic by-product emissions. Ongoing EPA research in this area and in real-time monitoring will be discussed. Real versus perceived concerns over thermal destruction will be put in perspective.

A PROFILE OF HAZARDOUS WASTE THERMAL DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS

By

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INTRODUCTION

Thermal destruction of hazardous waste involves the controlled exposure of waste to high temperature (usually 900°C or greater), and typically, an oxidizing environment. Thermal destruction processes include: thermal oxidation, starved air, or pyrolytic incineration systems; high temperature industrial processes such as boilers, cement kilns and industrial furnaces where hazardous waste is employed as a fuel; and various emerging processes which employ high temperatures, such as molten salt, plasma, or electric furnaces.

Properly designed and operated thermal destruction systems offer the prospect of destroying the hazardous organic components of waste streams while reducing waste volume and, in some instances, recovering energy or even materials such as hydrochloric or surfuric acid. Because of this, thermal destruction systems have emerged over the past decade as an increasingly desirable alternative to the more traditional hazardous waste disposal methods of landfilling, lagooning, and deep well injection.

However, improper design, operation, or use of such systems may also pose a threat to public health through emissions of potentially hazardous components of the waste or their combustion by-products. It was the recognition of the inherent environmental advantages of waste thermal destruction, balanced against the potential problems of improper practice that lead the U.S. Environmental Protection Agency (EPA) to develop performance standards and permit requirements for thermal destruction systems under the Resource Conservation and Recovery Act of 1976 (RCRA). Standards for incinerators have been in place since June 1982 (1) and standards are currently under development for disposal of hazardous wastes in industrial processes.

It is anticipated that thermal destruction will become even more important in the future as EPA responds to the Congressional mandate to restrict many hazardous wastes from land disposal and to effect corrective action at abandoned and uncontrolled disposal sites under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA or "Superfund").

The objective of this paper is to summary current thermal destruction practice in the United States including process configurations, facilities, wastes typically handled, and process performance data. In addition, several of the new more important technical and "non-technical" issues concerning the use of thermal destruction over the long-term will be discussed. EPA research designed to resolve these issues will be outlined.

CURRENT PRACTICES

The most recent comprehensive data on hazardous waste thermal destruction practice come from EPA surveys of industry activity in 1981. It is estimated that the United States generated 264 million metric tonnes (MMT) that year, a large portion of which was predominantly non-hazardous materials (water) contaminated with smaller amounts of hazardous materials (2). Over 5.5 MMT was managed by thermal destruction, with 1.7 MMT disposed in 240 incineration facilities and 3.8 MMT disposed in over 1300 industrial boilers and other industrial furnaces. EPA estimates that as much as 25 MMT of the waste generated in 1981 could have been directly managed by thermal destruction (3).

Hazardous waste incineration practice is more extensively documented than is waste disposal in industrial boilers and furnaces. Incinerators have been the subject of EPA research for nearly a dozen years. Regulation, notification, and permit requirements have also produced a larger data base on incinerators. The practice of waste disposal as a fuel in industrial boilers and other industrial process furnaces will not be fully regulated until early 1987.

Table 1 profiles United States incineration practice in 1981 (4). The most commonly used design is the liquid injection incinerator. These units, which are most frequently employed for disposal of waste at the site of generation, are applicable almost exclusively for pumpable liquid waste. They are usually simple, refractory-lined cylinders (either horizontally or vertically oriented) equipped with one or more waste burners. Liquid wastes are injected through the burner(s), atomized to fine droplets, and burned in suspension. Auxillary fuel burners as well as separate waste injection nozzles may be oriented for axial, radial, or tangential firing.

Fixed hearth incinerators, which include both excess air, starved air or pyrolytic incinerators, are the second most utilized technology for hazardous waste incineration. The starved air type, first marketed in the early 1960's, have seen rapid growth in use, particularly for on-site disposal of solid wastes.

Starved air incinerators are typically two-stage combustion processes where liquid or solid waste is fed into a primary chamber operated at 50 to 80 percent of the stoichiometric air requirement. Vaporized and partially destroyed combustion products are then directed to an afterburner where excess air is added to complete the destruction, usually at higher temperature than that employed in the primary chamber.

Rotary kiln incinerators are the third most used incinerator design. They are the most versatile incinerators in the sense that they are applicable to the destruction of solid wastes, slurries, and containerized waste as well as liquids. Because of this, these units are most frequently incorporated into commercial off-site incineration facility designs. Waste is volatilized and partially destroyed in the rotating kiln, a cylindrical refractory-lined shell

TABLE 1

UNITED STATES HAZARDOUS WASTE INCINERATION PRACTICES (1981)

OWNERSHIP:	80% private 20% commercial and military
WASTE:	77% of facilities handle on-site wastes only 79% of units - liquids only 11% of units - bulk wastes (solids and liquids) 10% of units - special purpose
EQUIPMENT:	48% are liquid injection units 19% are fixed hearth units 6% are rotary kiln or combination units 27% are other (military, fluid bed, etc.) 45% have air pollution control systems 22% employ heat recovery
OPERATIONS:	median - 1800°F at 2 seconds residence time (gas) range - 1200°F - 2300°F 0.1 seconds - 6.5 seconds residence time most operate on an intermittent schedule
CAPACITY:	median - liquids, 150 gal/hr solids, 650 lb/hr range - $0.3 - 142 \times 10^6$ = Btu/hr
MANUFACTURING:	57 companies actively marketing incinerators 28 companies sold units most units installed since 1970 32-40 units under construction

mounted on a slight incline. Combustion gases then pass through a high temperature afterburner to complete the destruction process.

The typical air pollution control system employed on hazardous waste incinerators include combustion gas quench, venturi scrubber (for particulate control), acid gas adsorber for acid gas removal (packed bed or tray-tower type), and a mist eliminator. It is interesting to note, however, that more than half of the incinerators in 1981 employed no air pollution control system at all. Ostensibly this reflects that these facilities were handling low ash, low halogen content liquid waste streams for which such control measures are not typically necessary.

Precise information on the exact types of wastes going to thermal destruction facilities is difficult to obtain. Many facilities operate on an intermittent basis and handle mixtures of wastes which are difficult to describe in terms of EPA standard waste codes. A 1983 EPA study examined data on 413 waste streams going to 204 of the 240 incineration facilities in the United States (5). The major waste streams incinerated were spent non-halogenated solvents (EPA waste code F003) and corrosive and reactive wastes contaminated with organics (EPA waste codes D002 and D003). Together these accounted for 44 percent of the waste incinerated. Other prominent wastes included hydrocyanic acid (P063), acrylonitule bottoms (K011) and contaminated water (D001).

Hazardous waste materials are also being burned as fuels in a wide range of industrial applications. In 1981 these operations disposed of more than twice the amount of waste which was disposed via incinerators. Processes that have burned or do burn hazardous waste materials as fuels include: industrial boilers, cement kilns, iron-making furnaces, light weight aggregate and asphalt plants. The principal attractions to this approach include: fuel and waste transportation cost-savings, and waste disposal cost savings since hazardous waste used as a fuel can be sold.

The most recent source of information on waste fuel use in industrial processes was compiled for EPA in 1984 (6). The study synopsizes results of a national questionnaire of waste fuel and waste oil use in 1983. The study revealed that there were over 1,300 facilities using hazardous waste-derived fuels (HWDF), accounting for a total of 230 million gallons per year. The chemical industry (Standard Industrial Classification 28 [SIC]) accounted for 67 percent of this while operating only 12.4 percent of the facilities using HWDF. Other industries employing significant quantities of hazardous waste as fuel included: SICs 26 (paper), 29 (petroleum), 32 (stone, clay, glass, concrete), and 33 (primary metals). The majority (69 percent) of waste was burned in large quantities by a few facilities representing only a fraction (1.6 percent) of the 1300 facilities. These included medium- to large-sized industrial boilers, cement and aggregate kilns, and iron-making furnaces.

While waste-code-specific data on HWDF are not readily available, recent data indicate that of the HWDF burned in 1983, 30 percent was organic solvents, and 45 percent was other hazardous organics (6). Most of this waste was generated on-site and 74 percent of the balance arrived directly from an off-site generator rather than an intermediary.

PERFORMANCE OF THERMAL DESTRUCTION DEVICES

Since 1980, the U. S. Environmental Protection Agency (EPA) has conducted waste destruction performance tests at nearly 50 full-scale hazardous waste thermal destruction facilities in the United States. The facilities tested have included:

- commercial and on-site incinerators
- incineration ships
- cement kilns
- industrial boilers
- commercial boilers
- light weight aggregate kilns
- steel blast furnace
- batch asphalt plants

The principal objective of these tests has been to characterize stack emissions and residues to determine if these facilities are capable of meeting the waste destruction and control requirements of current EPA regulations and standards. In the case of hazardous waste destruction, the incineration standards promulgated under the Resource Conservation and Recovery Act of 1976 (RCRA) are the required performance level for incinerators or chosen (other thermal destruction processes performance benchmark (1). These standards require that facilities must demonstrate that they can attain:

(1) 99.99 percent destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in the waste feed where:

$$DRE = (W_{in} - W_{out})/W_{in}) \times 100$$

Where: W_{in} = Mass feed rate of the principal organic hazardous constitutent (POHC) in the waste stream fed to the incinerator.

W_{out} = Mass emission rate of the POHC in the stack prior to release to the atmosphere.

(2) At least 99 percent removal of hydrogen chloride from the exhaust gas if hydrogen chloride stack emissions are greater than 1.8 kg/hr.

(3) Particulate matter emissions no greater than 180 mg/standard m^3 corrected to 7 percent oxygen in the stack gas. The measured particulate matter concentration is multipled by the following correction factor to obtain the corrected particulate matter emissions:

$$\text{Correction Factor} = 14/(21-Y)$$

Where: Y = measured oxygen concentration in the stack gas on a dry basis (expressed as a percentage).

The results of most of these performance tests have been compiled in published EPA reports and summarized in published papers (7-13). Tables 2, 3, and 4 describe the facilities and waste types encompassed by the test program and summarize waste destruction and emissions performance data. The data have shown that properly designed and operated incinerators, industrial boilers, cement kilns, and certain other industrial furnaces are capable of achieving or exceeding the RCRA DRE and hydrochloric acid gas requirements. The EPA also has conducted risk assessments using the emissions from the incinerators, boilers, and cement kilns tested. These assessments concluded that residual organic compounds in stack emissions posed no significant health risk (14-16).

TABLE 2

DESCRIPTION OF INCINERATION FACILITIES TESTED

FACILITY	CONTROL DEVICE	WASTE	DRE[a] (NO. OF NINES[b]	HCl CONTROL (AVERAGE)	AVERAGE PARTICULATE EMISSIONS (gr/dscf)
Commercial Rotary Kiln/ Liquid Incinerator (87 MM Btu/hr)	Packed Tower Adsorber Ionizing Wet Scrubber	Drummed, aqueous, liquid organic waste with carbon tetrachloride, TCE[c], perchloroethylene, toluene, phenol	5.3	99.4	0.67
Commercial Fixed Hearth, Two-Stage Incinerator (25 MM Btu/hr)	Electrified Gravel Bed Filter And Packed Tower Absorber	Liquid organic and aqueous waste with chloroform, carbon tetrachloride, TCE, toluene, perchloroethylene	4.4	98.3	.178
On-site Two-Stage Liquid Incinerator (6 MM Btu/hr)	Packed Tower Absorber	Liquid organic waste with carbon tetrachloride, dichlorobenzene, TCE, chlorobenzene, chloromethane aniline, phosgene	4.4	99.7	.027
Commercial Fixed Hearth, Two-Stage Incinerator (2 MM Btu/hr	None	Liquid organic waste with TCE, carbon tetrachloride, toluene, chlorobenzene	4.7	>4 lb/hr[d]	.089
On-Site Liquid Injection Incinerator (4.8 MM Btu/hr)	None	Liquid organic waste with aniline, diphenylamine, mono and dinitrobenzene	6.7	>4 lb/hr[d]	.092
Commercial Two-Stage Fixed Hearth Incinerator (10 MM Btu/hr)	None	Aqueous and organic liquid waste with carbon tetrachloride, TCE, benzene, phenol, perchloroethylene, toluene, methylethyl ketone	4.8	>4 lb/hr[d]	.40
On-site Rotary Kiln With/ Liquid Injection (35 MM Btu/hr)	Venturi Scrubber With Cyclone Separators And Packed Tower Absorbers	Liquid organic, point waste and filter cakes with methylene chloride, chloroform, benzl chloride, hexachloroethane, toluene, TCE, carbon tetrachloride	5.3	99.9	.01
Commercial Two-Stage Fixed Hearth Incinerator (75 MM Btu/hr	Venturi Scrubber	Aqueous and organic liquids and solid waste with methylene chloride, chloroform, carbon tetrachloride, hexachlorocylopendtadiene, toluene, benzene, TCE	4.6	98.3	.075

(a) Destruction and Removal Efficiency (Mass Weighted Average For All POHCs >100 ppm In Waste Feed)
(b) For Example, 99.995 Percent DRE = 4.5 nines
(c) TCE = Trichloroethylene
(d) No HCl Control Device, Waste Low In Total Organic Chlorine Content

TABLE 3

DESCRIPTION OF INDUSTRIAL BOILER FACILITIES TESTED

ACILITY	CONTROL DEVICE	WASTE	DRE(a) NUMBER OF NINE(b)
(1) Watertube Stoker - wood-fired (10 MMBtu/Hr)	Multiclone	Creosote Sludge With Phenol Pentachlorpheno And Napthalene	3.8
(2) Packaged Firetube - gas-fired (8.5 MMBtu/Hr)	None	Alkyd Wastewater With Toluene	4.1
(3) Field Erected Watertube - gas/oil-fired (230 MMBtu/Hr)	None	Phenol Waste	5.6
(4) Converted Stoker - oil-fired (90 MMBtu/Hr)	None	Methanol, Toluene And Chlorinated Organics Including Perchloroethylene	4.8
(5) Packaged Watertube - oil-fired (110 MMBtu/Hr)	None	Methyl Methacrylate By-products With Carbon Tetrachloride, Chlorobenzene And TCE(c)	4.5
6) Converted Watertube - oil-fired (60 MMBtu/Hr)	None	Paint Solvents With Carbon Tetrachloride, TCE, Toluene And Chlorobenzene	3.8
7) Modified Firetube - waste-fired (40 MMBtu/Hr)	2 Scrubbers In Series	Highly Chlorinated Organics Including Carbon Tetrachloride	4.8
8) Tangentially Fired Watertube - coal-fired (250 MMBtu/Hr)	ESP	Methyl Acetate, Carbon Tetrachloride, Trichloroethane Chlorobenzene	4.1
9) Packaged Watertube - gas-fired (62 MMBtu/Hr)	None	Aniline Waste With Nitrobenzene, Carbon Tetrachloride, TCE, Benzene, Toluene	4.8
10) Packaged Firetube - waste-fired (10 MMBtu/Hr)	None	Toluene, Chlorinated Organics, Including Carbon Tetrachloride, TCE	5.0
11) Packaged Watertube - oil-fired (60 MMBtu/Hr)	None	Blended Waste With Light Oil And Carbon Tetrachloride, Benzene, TCE, Toluene	5.7

a) Destruction And Removal Efficiency (DRE), Mass Weighted Average of POHCs >100 ppm in Waste Feed
b) For Example, 99.995 Percent DRE = 4.5 Nines
c) TCE = Trichloroethylene

TABLE 4

DESCRIPTION OF INDUSTRIAL KILNS FACILITIES TESTED

FACILITY	CONTROL DEVICE	WASTE	DRE(a) NUMBER OF NINES)(b)
(1) Wet Process Cement Kiln Non-atomized Waste 140 MMBtu/Hr - oil fired	Fabric Filter	Waste Liquids Including, Methylene Chloride, Chloroform, Carbon Tetrachloride	2.8
(2) Wet Process Cement Kiln Atomized Waste 170 MMBtu/Hr - coal fired	ESP	Waste Liquids, Including Methylene Chloride, MEK, Trichloroethane, Toluene, Freon 113	4.2
(3) Dry Process Cement Kiln Non-atomized Waste 228 MMBtu/Hr - coal/coke fired	ESP	Waste Liquids, Including Methylene Chloride, Freon 113, MEK, Toluene, Trichloroethane	4.1
(4) Dry Process Cement Kiln Atomized Waste 300 MMBtu/Hr - coal/coke fired	Fabric Filter	Waste Liquids, Including Trichloroethane Trimethylbenzene, Xylene, Methylene Chloride	>4
(5) Lime Kiln Atomized Waste 50 MMBtu/Hr - coke/gas fired	Fabric Filter	Waste Liquids, Including Methylene Chloride, MEK, Trichloroethylene	4.7
(6) Shale Aggregate Kiln Atomized Waste 35 MMBtu/Hr - coal fired	Scrubber	Waste Liquids, Including Perchloroethylene, Methylethyl	>5
(7) Clay Aggregate Kiln 20 MMBtu/Hr - coal fired	Scrubbers	Waste Liquids, Including Methylethyl Ketone, Perchloroethylene And Toluene	4.8
(8) Clay Products Kiln Atomized Waste 37.5 MMBtu/Hr - oil fired	Fabric Filter	Waste Liquids, Waste Oil, Freon 113. Perchloroethylene Carbon Tetrachloride, Benzene, TCE, Toluene	3.5

(a) Destruction And Removal Efficiency (DRE), Numerical Average Of Major POHCs
(b) For Example, 99.995 Percent DRE = 4.5 Nines
(c) MEK = Methyethyl Ketone

Remaining Issues

While thermal destruction represents the most effective and widely applicable control technology available today for organic hazardous waste, a number of issues remain concerning its use in the long term. These include:

- Destruction effectiveness on untested/unique wastes
- Detection of process failure
- Control of heavy metal emissions
- Emissions of combustion by-products
- Available thermal destruction capacity
- Permits and public acceptance

The balance of this paper will attempt to define each of these issues more fully, present applicable data and other information to put these concerns into some perspective, and summarize ongoing EPA research designed to improve our understanding in these areas.

Untested Wastes

All of the performance data which have been used in the development and assessment of thermal destruction regulations and standards have obviously been collected for waste/thermal-technology combinations typical of current practice. However, the character of wastes which may be subjected to incineration in the near future will begin to change, perhaps dramatically. These changes will be influenced by EPA action to restrict many wastes from land disposal under the Hazardous and Solid Waste Act Amendments of 1984 (HSWA) and by increased emphasis upon remedial action at "Superfund" sites. Incineration will emerge as a feasible technological alternative for destruction of many of these wastes and site clean-up residues. However, EPA and industry will have considerably less experience in handling these wastes. They will tend to have higher solids and water content, be more complex in their physical and chemical composition, have lower heat content, and potentially contain higher levels of hazardous metals and high hazard organics compared to wastes which are typically incinerated today.

Consequently, while incineration is capable of achieving high levels of destruction for today's wastes, future wastes may place new performance demands on current technology. For instance, 99.9999 percent DRE is now required for wastes bearing chlorinated dioxin and furan compounds. Many of these wastes appear at Superfund sites. EPA is also studying the need for heavy metals control regulations for incinerators. That effort may suggest the need for improved air pollution control systems or waste pretreatment. Thus, performance testing of incinerators and other thermal destruction devices must continue in order to assure destruction and removal effectiveness for these untested wastes, to assess process limitations and waste pretreatment requirements, determine the safety of process residues, and to improve our ability to predict performance on new waste materials.

Detection Of Process Failure

While well-operated thermal destruction facilities achieve high levels of organic hazardous material destruction, little is known about the impact of process upsets or failure modes upon emissions. This is often a concern of the public in hearings and permit actions.

While convincing trial burn performance data can be presented, uncertainty and distrust may exist regarding the reliability of thermal destruction systems in day-to-day operation after a permit is approved and when regulators are not present.

Currently, permit conditions are primarily based upon process operating conditions which are documented during the conduct of a successful trial burn; i.e., one which demonstrated that the facility achieved or exceeded the RCRA performance standards. Operating conditions (e.g., combustion temperature, O_2, and CO in stack emissions, etc.) must be used as surrogates for similar high performance after the fact since there is currently no real-time method to determine DRE for specific POHCs. DRE can only be determined with certainty via expensive, often multi-day testing procedures. Analysis results may take weeks or months to complete. While EPA believes this approach is reasonable and protective of public health and the environment, many argue that the availability of a real-time monitoring technique to detect process upsets and alert operators to automatically take corrective action would significantly increase public acceptance of thermal destruction technology.

EPA is currently conducting extensive research to assess the impact of the most likely process failure modes upon performance. The failure conditions being studied include: improper waste atomization; overfeeding or unstable feeding of waste; inadequate combustion temperature; post-combustion quenching of destruction reactions; inadequate combustion mixing; and a variety of other process-specific variables. This research is being conducted in laboratory- and pilot-scale incineration systems at EPA facilities in Cincinnati, Ohio, Research Triangle Park, North Carolina, and Jefferson, Arkansas. The experimentation is attempting to correlate process failure with a variety of potential performance indicators which can be inexpensively measured more or less instantaneously. The indicators currently being examined include: total unburned hydrocarbon emissions (TUHC); carbon monoxide emissions (CO); oxygen levels in stack emissions (O_2); and emissions of tracer compounds such as sulfur hexafluoride and various freons which could be added to a waste stream and be monitored as a potential surrogate for other organic compound destruction.

Results to date have not conclusively shown a universal correlation of any of the performance indicators with DRE. It appears that such correlations may be very waste and facility specific. TUHC and CO emissions appear to hold the most promise. As the research progresses, EPA hopes that statistical and engineering analysis will reveal a reliable approach which could be used during the trial burn to calibrate individual facilities for a DRE/surrogate relationship. The appropriate monitor could then be used for process control or compliance monitoring during normal operation.

Metal Emissions

Metals such as arsenic, barium, beryl1uim, chromium, lead, mercury, nickel, and zinc are of possible concern in waste incineration because of their presence in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form but not the content of metal fractions in waste streams. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental control concern therefore centers around where and in what physical or chemical form the metals partition in the combustion system, i.e., bottom ash, fly ash, in APCD residues, or stack emissions.

The primary controller for metals emissions from incineration is the RCRA particulate emission standard of 180 mg/dry standard cubic meter. Half of the incinerators evaluated in EPA's incinerator testing program (4 of 8) failed to meet this standard. Two of the facilities which failed did not have particulate pollution control systems. The other two units employed somewhat dated and poorly-maintained systems. Similar results are also being observed in trial burn data being submitted to EPA in permit applications.

Data were collected on actual metal emissions during the EPA incinerator testing program, as well as during certain of the other facility tests (cement kilns, waste oil combustion, boilers). As part of EPA's Regulatory Impact Assessment performed to examine the impact of the regulations on the regulated community and to examine the health and environmental effects of the regulation, the risks due to emissions of principal organic hazardous constituents (POHCs), combustion by-products (PICs), and metals were developed and presented for incinerators (14). The overall summary of results is presented in Table 5.

TABLE 5. Total excess lifetime cancer risk to the maximum exposed individual for incinerator emissions

POHCs	10^{-7} to 10^{-10}
PICs	10^{-7} to 10^{-11}
Metals	10^{-8} to 10^{-5}
TOTAL	10^{-8} to 10^{-5}

The risks from metals emissions ranged from two to six orders of magnitude higher to one order of magnitude lower than from POHCs and PICs, and dominated the total risk values.

The risk estimates for metals were based on emission measurements from the stack sampling program conducted during the tests. The metals analyses were conducted on the particulates collected during stack sampling. The risk analysis for metals was conducted in two parts; for metals exhibiting carcinogenic properties, and for non-carcinogenic effects (threshold) for a range of metals.

While these results show that the health risks of most wastes in most incinerators are low, risks from metal emissions show the greatest potential for exceeding a 10^{-6} cancer risk. This is particularly true for facilities which may be operating at or near the RCRA particulate emission standard or those which may wish to incinerate waste higher in metal content in the future.

EPA is considering various regulatory options for controlling metal emissions from hazardous waste thermal destruction facilities. To support the development of these potential regulations, research is underway to assess the character and fate of metals in incineration systems as a function of incinerator design and operation, waste characteristics and air pollution control system operation. Testing in pilot-scale incinerators will be conducted at EPA's Combustion Research Facility in Jefferson, Arkansas to develop metal partitioning models for conventional incineration system configurations. These models will be verified in field tests of commercial systems. The waste impact of pretreatment or improved air pollution control systems will be assessed in the research program.

Combustion By-Product Emissions

The current RCRA incineration standards regulate destruction and removal only for the major hazardous compounds in the waste. One of the concerns expressed by scientists and environmentalists regarding hazardous waste thermal destruction is the possible impact on human health and the environment of emissions of potentially hazardous products of incomplete combustion or PICs. This concern prevails in spite of the fact that EPA assessments have indicated that the risks from PIC emissions are low. In case of incinerators, Table I shows that the total excess lifetime cancer risk to the maximum exposed individual are essentially the same for PICs and POHCs, and both are less than 10^{-7}. Analysis of emissions data from tests of hazardous waste destruction in industrial boilers revealed that risks from PICs were consistently higher than POHC emission risks, but that neither risk was ever greater than 10^{-6} (16).

One basic issue which remains unresolved is the definition of a PIC. While a POHC is defined in the RCRA regulations, a PIC is not in a rigorous sense. Thus, there is often confusion even among scientists working in the area. Strictly speaking, PICs are organic compounds which are present in the emissions from the combustion process, which were not present or detectable in the fuel or air fed to the combustor. In EPA's test program, compounds were considered to be PICs if they were regulated organic compounds (i.e., listed in Appendix VIII of CFR 40 Part 261) which were detected in stack emissions, but not present in the waste feed at concentrations greater than 100 ppm.

Compounds in the emission stream which are identified as PICs can actually be any one of the following:

1. Compounds resulting from the incomplete burning of the principal organic hazardous constituents (POHCs), i.e., fragments of the original POHCs.

2. New compounds "created" in the combustion zone and downstream as the result of partial destruction followed by recombination with other compounds or fragments present.

3. A compound originally present in the feed stream before combustion but not specifically identified as a POHC.

EPA field studies of thermal destruction systems have identified 55 Appendix VIII compounds (28 volatile and 27 semi-volatile) in stack emissions (7,8,11). These compounds were emitted at rates that span over five orders of magnitude, 0.09 to 13,000 nanograms of emissions per kilojoule of combustor heat input [ng/kJ]. The volatile compounds tended to be detected more often and in significantly higher concentrations than the semivolatile compounds. The compounds that occurred most frequently and in the highest concentrations, nine volatile and six semivolatile, are listed in Table 6.

In a recent study (18), a subset of the available data was defined which consisted of only those data where specific compounds were identified in stack emissions but not in the waste burned (i.e., PICs). These data were used to compare emissions from incinerators, boilers, and kilns as shown in Table 7. Three of the semivolatile compounds listed earlier were not included because there was minimal data for comparison. The data in Table 7 show that values from test run to test run varied considerably, thus these data do not allow prediction levels for all three combustion devices. Many of the volatile compounds showed higher levels for boilers, and incinerators tended to show higher levels for semivolatiles.

TABLE 6. Most frequent thermal destruct process stack emissions

VOLATILE COMPOUNDS	SEMI-VOLATILE COMPOUNDS
Benzene	Naphthalene
Toluene	Phenol
Carbon tetrachloride	Bis(2-ethylhexy)phthalate
Chloroform	Diethylphthalate
Methylene chloride	Butylbenzylphthalate
Trichloroethylene	Dibutylphthalate
Tetrachloroethylene	
1,1,1-Trichloroethane	
Chlorobenzene	

Data were also available from several baseline (no waste firing) tests on boilers and kilns. The fuel for most of the baseline tests was oil or natural gas, with some coal burned in a few kiln tests. These data were used to compare emissions from hazardous waste combustion with combustion of fuel without hazardous waste. Table 8 presents this comparison for volatile compounds. Sufficient data were not available for a similar comparison for semi-volatile compounds. Considering the wide range in values from test to test, the data

TABLE 7. Emission rates of specific compounds from incinerators, boilers, and kilns, ng/kJ

	Incinerators		Boilers		Kilns	
	Mean	Range	Mean	Range	Mean	Range
Benzene	87	2-980	30	0-300	580	290-1,000
Toluene	1.6	1.5-4.1	280	0-1,200	----	No data ----
Carbon tetrachloride	0.8	0.3-1.5	1.8	0-7.2	----	No data ----
Chloroform	3.8	0.5-8.4	120	0-1,700	----	No data ----
Methylene chloride	2.2	0-9.6	180	0-5,800	----	No data ----
Trichloroethylene	5.2	2.3-9.1	1.2	0-13	1.3	0.7-2.8
Tetrachloroethylene	0.3	0-1.3	63	0-780	----	No data ----
1,1,1-Trichloroethane	0.3	0-1.3	7.5	0-66	2.4	(One value)
Chlorobenzene	1.2	0-6.0	63	0-1,000	152	33-270
Naphthalene	44	0.7-150	0.6	0.3-2.1	----	No data ----
Phenol	7.8	0-16	0.3	0-0.8	0.02	0-0.05
Diethylphthalate	3.7	2.8-4.8	0.4	0.04-1.6	----	No data ----

in Table 8 suggest there is little inherent difference between waste and fuel combustion in emissions of the volatile compounds shown in the Table.

Sufficient data for five semivolatile compounds were available to compare their emissions when burning hazardous waste versus their emissions from municipal incinerators and coal-fired power plants. Similar data were not available for volatile compounds. Table 9 presents this comparison. The four phthalate compounds in the Table all show very similar emission rates from all three sources. Naphthalene emissions were lower for power plants then the other two sources. Again, the data suggests that for some compounds there is little inherent difference between combustion sources.

An additional concern many have expressed regarding the issue of PICs is that EPA risk assessments have been limited to only metals and the Appendix VIII organic compounds. Comparison of total hydrocarbon emissions with the total quantity of organic compounds emitted has revealed that only a relatively small percentage of the total hydrocarbon emissions have been identified (Table

TABLE 8. Volatile compound emission rates from hazardous waste and fuel combustion, ng/kJ

	Waste		Fuel	
	Mean	Range	Mean	Range
Benzene	120	0-1,000	320	0-1,100
Toluene	210	0-1,200	190	0-1,500
Chloroform	90	0-1,700	14	0-800
Methylene chloride	130	0-5,800	160	0-3,400
Trichloroethylene	1.8	0-13	1.5	0-14
Tetrachloroethylene	49	0-780	7.7	0-52
1,1,1-Trichloroethane	5.6	0-66	1.7	0-14

10). This has raised the question of what other potentially hazardous compounds (Appendix VIII or non-Appendix VIII) might remain in the unidentified emissions and what additional risk these might pose.

EPA has had some of the incinerator test analyses reviewed to identify additional compounds (18). This review showed that the quantity of volatile non-Appendix VIII compounds detected by GC/MS varied from only a fraction of the total quantity of Appendix VIII compounds in one case to twice the quantity in another case. For semi-volatiles, the search showed that the total of non-Appendix VIII compounds was 3 to 30 times the quantity of Appendix VIII compounds. Some of the non-Appendix VIII compounds identified in the highest concentrations were:

Acetone
Acetophenone
Benzaldehyde
Benzenedicarboxaldehyde
Benzoic acid
Chlorocyclohexanol
Cyclohexane
Cyclohexanol
Cyclohexene
Dioctyl adipate
Ethenylethylbenzene
Ethylbenzaldehyde
Ethylbenzene
Ethylbenzoic acid
Ethylphenol
(Ethylphenyl)ethanone
Ethenylbenzene
Phenylacetylene
Phenylbutenone
1,1'-(1,4-Phenylene)-bisethanone
Phenypropenol
Propenylmethylbenzene
Tetramethyloxirane
Trimethylhexane

TABLE 9. Semi-volatile compound emission rates from hazardous waste combustion, municipal incinerators, and coal power plants, ng/kJ

	Hazardous waste		Municipal waste		Coal power plant	
	Mean	Range	Mean	Range	Mean	Range
Naphthalene	17	0.3-150	71	0.4-400	0.5	0.06-1.8
Bis(2-ethylhexyl)phthalate	4.6	0-21	4.6	0.4-12	7.6	0.2-24
Diethylphthalate	1.2	0.04-4.8	0.5	0.0.9	2.8	0.4-5.7
Butylbenzyphthalate	3.7	0.7-23	-- No data ----		0.5	0.3-1.0
Dibutylphthalate	0.3	0-1.1	3.9	1.5-7.6	3.0	0.09-8.7

TABLE 10. Total appendix VIII compounds measured as percent of total hydrocarbon

	Mean	Range
Incinerators	12	0.3-44
Boilers	0.4	0.01-1.1
Kilns	14	0.1-50

The EPA Science Advisory Board has reviewed the available emissions data for incinerators. While they have concluded that incineration is an effective destruction technology, they also concluded that a complete risk analysis was limited by an incomplete knowledge of the full range of compounds which are emitted from the stack during thermal destruction of hazardous waste (19). To address this issue, EPA will conduct an emissions test at a full-scale hazardous waste incinerator in the Fall of 1986 in an effort to quantify total mass emissions (TME). The project will employ a broader array of sampling and analysis techniques than used in previous testing. The difference between steady-state operation and operation with typical transient conditions will also be studied. It is hoped that this test will characterize emissions sufficiently to allow a complete risk assessment and verify previous conclusions on risks.

Capacity

There has been considerable discussion recently regarding the need for increased hazardous waste thermal destruction capacity in the United States.

This issue is important for two reasons. First, thermal destruction is being identified by EPA as best demonstrated available technology for many of the wastes which will be restricted from land disposal under HSWA. The dates when restrictions on specific waste streams become effective will be, in part, a function of the availability of permitted thermal destruction capacity to handle the amount of waste expected to be diverted from land disposal.

Capacity is also an issue in the issuance of permits to incinerate hazardous wastes at sea in specially-designed incineration ships. Approval of disposal at sea is, in part, dependent upon successfully demonstrating a sufficient need to do so (i.e., insufficient land-based capacity).

EPA has conducted several studies of thermal destruction capacity over the past several years (17,20,21). The most recent data on incinerator capacity is summarized in Table 11. There are 208 operating incinerator facilities in the United States. Of these, 34 have final operating permits and 174 have filed final applications which are being evaluated. Design capacities were obtained for 87 percent of the 208 units. The design, or nameplate, capacity of these reporting units is 6.28 billion Btu/hr. Extrapolating this statistic to include all 208 incinerators subject to the RCRA regulatory program, the national capacity could be 7.2 billion Btu/hr, which is equivalent to approximately three (3) million metric tonnes of hazardous waste per year. Fume incinerators which are incinerating liquid hazardous waste appear to be approaching their capacity (94 percent), followed by rotary kiln incinerators (77 percent).

TABLE 11. Estimation of available hazardous waste incinerator capacity by incinerator design

INCINERATOR DESIGN	NUMBER OF UNITS	AVERAGE DESIGN CAPACITY (Million Btu/hr)	UTILIZATION (Percent)	AVAILABLE CAPACITY (Million Btu/hr)	PERCENT WITH AIR POLLUTION CONTROL EQUIPMENT
Rotary Kiln	42	58.7	77	570	90
Liquid Injection	95	36.1	55	1540	42
Fume	25	29.5	94	40	40
Hearth	32	22.5	62	270	38
Other	14	23.8	--	110	--
Total or Average Values	208	37.6*	67**	2530	50

*181 incinerators reporting
** 90 incinerators reporting

The study also revealed that since 1981, almost 100 incinerators had withdrawn from the RCRA system because they either ceased operation or were no longer handling hazardous wastes. Also, of the 57 companies identified as marketing hazardous waste incinerators in 1981, 23 have either gone out of business, left the hazardous waste incinerator business, or put considerably less emphasis on this activity. Only one new company is pursuing this market. Apparently, many of the companies that were anticipating large growth in the incineration market in 1981 have abandoned the business as a result of selling only a few or no units since then. The remaining 35 manufacturers, however, reported that 111 new incinerators had been sold since 1981.

It is believed that 12 cement kilns have received the hazardous waste storage permits necessary to burn hazardous waste as a fuel in their processes (22). This corresponds to a capacity of between 87,000 tonnes of waste per year. These estimates are one to four percent of the estimated potential cement kiln capacity. The available capacity estimates for wastes that could be destroyed in cement kilns range from two (2) to six (6) million tonnes per year, or from 0.8 to 2.3 percent of the hazardous waste generated annually in the United States.

There are also over 43,000 industrial boilers in the United States of sizes and designs which are potentially able to achieve acceptable waste destruction.[7] Of this population, 5,500 boilers are located in the chemicals, petroleum refining, and paper industries. These boilers are accessible to about 70 percent of total hazardous waste generated and over 95 percent of all potentially combustible hazardous waste, and are the most likely boiler candidates for waste firing. EPA estimates that approximately 1300 boilers are actually disposing of 3.5 million tonnes of hazardous waste annually (13). If the remaining 4,200 boilers in the chemicals industry were to begin using hazardous waste as fuel at an equivalent rate, this quantity could increase to 14.8 million tonnes/year.

The conclusion one draws from these data is that, in the very near term, there appears to be sufficient thermal destruction capacity in the United States (Table 12). In addition, if permits are granted for the two Vulcanus seabased incinerators, incineration capacity for liquid wastes could increase by 100,000 tonnes per year.

EPA has estimated the amount of hazardous waste which might be redirected to commercial incineration as a result of restrictions upon disposal in landfills, lagoons, and injection wells (21). Each of these three restriction scenarios are projected to result in an excess of commercial incineration demand over existing capacity of 215 to 306 percent for liquid wastes alone. Translated into facilities, this converts to as many as 26 incinerators (20,000 tonnes each). Solid hazardous waste and Superfund clean-up residues would further increase the shortfall.

While there are many boiler and kiln facilities which could dispose of waste, much of the waste which will become available for use in these thermal destruction facilities in the future is likely to be increasingly less attractive to them. This waste will tend to be much less combustible and higher in solids, ash, and water content and, therefore, more suited to more conventional commercial incineration facilities. Thus, unless the rate of commercial incineration

TABLE 12. United States thermal destruction capacity for hazardous waste (million tonnes per year)

Facility Type	Current Utilization	Capacity	% Utilization
Incinerators (land-based)	1.7	2.7	63
Industrial Boilers	3.5	14.8	24
Cement Kilns	0.9	2-6	15-45
Incinerators (ocean)	0	0.1	0

facility permitting and construction increases (particularly for solid hazardous wastes) the effective capacity may well be insufficient for new wastes which will enter the system from land disposal restriction and Superfund clean-up activities.

Permits And Public Acceptance

While thermal destruction offers many advantages over existing hazardous waste disposal practices and may help to meet the anticipated need for increased waste management capacity, public opposition to the permitting of new thermal destruction operations has been strong in recent years. The normal time required for permitting new incineration facilities is three years. This time as well as the expense of obtaining a permit may be greatly increased if public opposition exists.

The amount of public opposition to proposed permits for land-based incinerator facilities varies by location and type of waste. On-site facilities that directly serve a single waste generator have greater public acceptance than off-site commercial incinerators that serve multiple generators in a large market area. Off-site facilities are often not perceived as providing sufficient economic benefits to the local community to offset the risks associated with the importation of wastes from other areas. On-site facilities are more clearly perceived as being linked to businesses that are important to the local economy, and are generally not perceived as being importers of hazardous waste. Opposition has tended to focus primarily on new off-site facilities, including incinerator ships, and on new applications to burn PCBs, which critics view as particularly hazardous.

In an effort to assess the dilemma of perceived benefits versus public concerns, EPA conducted an assessment in 1985 to determine if there was a need for a change in the Agency's approach toward regulating thermal destruction (23). The major concerns reported by citizens included:

- Hazardous material spills in storage, treatment, and handling.
- Environmental and health impacts of land-based and ocean facilities.
- Poor site selection processes.
- Distrust of incinerator owners and operators.
- Inability of government agencies to enforce compliance.

The study concluded that public opposition to both land and ocean incineration may decline somewhat if EPA addresses more fully some citizen concerns regarding national regulatory strategy, local community impacts, equity of facility siting, public decision-making processes, and especially enforcement plans and capacity. There is a need to better communicate how health and environmental concerns and priorities are reflected in the Agency's regulations and standards. Better communication of EPA's overall regulatory policy, strategy, and activities for decisions on proposed permits for individual incinerator facilities or vessels is needed. Better public communication is also important for improving EPA's credibility with the public, which is a necessary foundation for the effective accomplishment of the Agency's mission.

CONCLUSIONS

Thermal destruction of hazardous waste in incinerators and certain industrial processes represents the most effective technique currently available for organic wastes. While current assessments reveal that the emissions of metals and hazardous organics from these facilities present no significant health risks, a variety of scientific and public concerns remain over their safety. EPA is striving to improve our understanding of thermal destruction through a full range of ongoing research designed to answer the remaining concerns and bolster public confidence in thermal destruction. This research includes investigations into the development of real-time indicators of incinerator performance, performance tests on untested and high hazard wastes streams, and assessments of the impact of thermal destruction process upsets on emissions of metals and incomplete combustion by-products.

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HAZARDOUS WASTE LANDFILL RESEARCH

U.S.E.P.A. PROGRAM

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INTRODUCTION

The Land Pollution Control Division (LPCD), Hazardous Waste Environmental Research Laboratory (HWERL), U.S. Environmental Protection Agency (USEPA), in Cincinnati, Ohio, has responsibility for research in solid and hazardous waste management with respect to land disposal of wastes. To fulfill this responsibility, the LPCD is developing concepts and technology for new and improved control systems for solid and hazardous waste land disposal; is documenting the environmental effects of various waste disposal practices; and is collecting data necessary to support implementation of disposal guidelines mandated by The Hazardous and Solid Waste Amendments of 1984 (HSWA). This paper will present an overview of the land disposal research associated with the LPCD hazardous waste program plan.

The performance of treatment, storage, and disposal facilities are being improved to contain the complex wastes being generated by a changing society. These improvements are brought about by the development of control technologies which are useful to the USEPA program offices, Office of Solid Waste (OSW) and Regions, state and local agencies, design engineers and waste management facility operators. The results of these improved control technologies will be the ability to optimize designs, minimize maintenance and overall costs while maintaining a high degree of confidence that the waste management facility will operate as designed. The control technologies being developed or improved take into account region uniqueness, complex waste streams including quality, quantity, and physical state, and a variety of potential designs which will minimize/prevent releases to the environment from waste disposal facilities. These technologies are being laboratory-studied and field-verified to provide the user community with economical, long-lasting systems that will contain the changing waste streams that are being disposed of by traditional, innovative, and high technology industries.

This paper will present an overview of the land disposal research associated with the LPCD hazardous waste program plan and will report the current status of work in the following categorical areas:

HAZARDOUS WASTE FACILITIES - LANDFILLS AND SURFACE IMPOUNDMENTS

1. Cover Systems
2. Waste Leaching/Modification
3. Flexible Membrane Liners
4. Clay Soil Liners
5. Quality Assurance/Quality Construction
6. Expert Systems
7. Corrective Action

NON-HAZARDOUS WASTE FACILITIES

1. Subtitle "D" Facilities

TECHNOLOGY TRANSFER

1. Technical Research Documents

HAZARDOUS WASTE FACILITIES - LANDFILLS AND SURFACE IMPOUNDMENTS

COVER SYSTEMS

The objective of this activity is to develop and evaluate the effectiveness of various cover systems in relation to their functional requirements for actual field application. The primary functional requirements are to minimize moisture infiltration and to promote gas venting. Validation efforts are being performed in the laboratory and field with model work development being pursued for eventual incorporation into a Technical Resource Document (TRD).

The inital laboratory efforts on the study of landfill cover performance have been completed. These recently completed efforts focused on multi-layered cover systems utilizing materials such as a variety of soils, flexible membrane liners and sand drainage blankets. Additional studies may become necessary depending on the results obtained from current field and modeling investigations.

The field efforts being investigated are concerned with the monitoring and modeling of the hydrologic integrity of three multi-layered landfill covers under stable and subsidence conditions. This study monitors infiltration conditions within the constructed cover soil layers and then applied soil moisture, precipitation, and runoff data to verify hydrologic models such as "The Hydrologic Evaluation of Landfill Performance" (HELP) and "The Chemicals, Runoff, Erosion and Agricultural Management System" (CREAMS).

The TRD is a compilation and presentation of best available technology and information on methods to control infiltration, to improve long-term cover performance and on the development of construction, maintenance, and inspection criteria to improve clay and flexible membrane cover performance, cover drainage and maintenance free vegetative cover systems. The initial TRD entitled, "Design, Construction, and Maintenance Cover Systems for Hazardous Waste" was published in 1984. This document can be ordered from the National Technical Information Service (NTIS). The NTIS stock number is PB81-166-340. This TRD is currently being updated and should be available for publication in the spring of 1987. A technical handbook entitled, "Covers for Uncontrolled Hazardous Waste Sites" EPA/540/2-85/002 dated September 1985 has been published under the Superfund program. This technical handbook provides guidance for regulatory personnel involved with Superfund sites but could be also used at other controlled sites.

WASTE LEACHING/MODIFICATION

The objective of this activity is twofold: (1) to develop and evaluate laboratory techniques for working with a sample of a waste or a mixture of waste to predict the composition of actual leachates obtained under field conditions and (2) to evaluate the effectiveness of solidification/stabilization and encapsulation processes for improved handling, surface area reduction, limiting solubility, detoxifying pollutants and predicting performance with time. Results from laboratory and model predictions are being compared with results from pilot-scale and field-scale work to develop better evaluation procedures and an up-dated TRD on waste leaching and waste modification.

The laboratory efforts currently being pursued relating to waste modification include the study of solidification/stabilization mechanisms, whether due to physical entrapment or chemical interaction. This effort is determining in what phase(s) of the binder-waste matrix the contaminants are held. Microscopy and leaching procedures are used with organic and inorganic wastes. In addition, various solidification/stabilization processes are being assessed and evaluated to determine the effects of interfering materials (organics and inorganics) on process and product performance. Evaluation of the waste modification techniques includes leaching to determine concentrations of contaminants released and physical measurements (e.g., freeze-thaw, wet-dry) to assess durability of the solidified waste.

Currently no field efforts are being pursued in this research area. Future studies may become necessary depending on the results obtained from current investigations.

The original TRD on "Solid Waste Leaching Procedure" (SW-924) has been updated and a 2nd edition entitled, "A Procedure for Estimating Monofilled Solid Waste Leachate Composition" (SW-924) is being reviewed by OSW. Final publication is expected by March 1987. In addition to the leaching procedure TRD, a TRD entitled, "Landfill and Surface Impoundment Performance Evaluation" (SW-869) relating to leachate generation was published in 1984 and can be obtained from the NTIS. PB81-166-357 is the NTIS stock number. The original TRD on "Guide to the Disposal of Chemically Stabilized and Solidifed Wastes" (SW-872) was published in 1984 and can be ordered from NTIS. The NTIS stock number is PB81-166-505.

This original stabilization TRD has been updated as a technical handbook for Superfund sites. This document entitled, "Handbook for Stabilization/Solidification of Hazardous Wastes," EPA/540/2-86/001 dated June 1986 has been published.

FLEXIBLE MEMBRANE LINERS

The objectives of this activity are to evaluate the effectiveness of synthetic membranes or flexible membrane liners (FML's) as liners and surface caps to contain or minimize leachate movement and prevent moisture infiltration, and to develop means to predict the long-term performance of liners.

The laboratory efforts include the evaluation of upward hydrostatic forces on FML's and loading points and also for the development of field verification data for flexible membrane liners (FML's). The research of upward hydrostatic forces is evaluating the puncturability effects of fixed point loads in a subgrade under slowly increasing water pressure. Room and elevated temperatures are being used to accelerate the potential reaction. The benefits of using geotextiles to prevent the puncture are also being evaluated.

The effort to develop field vertification data for FML's has met with limited success. Results indicate laboratory tests, such as Method 9090, can predict the chemical compatibility of FMLs. However, additional field data are required to assess long-term performance and environmental stress cracking.

A major revision of the TRD (SW-870) "Lining of Waste Impoundments and Disposal Facilitlies" is underway. New information is now available on improved techniques for estimating chemical compatibility, seam quality, and understanding field failure mechanisms. The very rapid increase in use of geotextiles and geonets in lining systems necessitates a major revision to the TRD to include these topics. The draft revision is scheduled for the fall of 1987 with final publication in early 1988.

CLAY SOIL LINERS

The objective of this activity is to evaluate the effectiveness of compacted clay soils used in surface covers and bottom liners for minimizing infiltration of water and escape of leachate. Results of these laboratory and field evaluations are then used to develop procedures for evaluating designs and predicting long-term performance so that liners can be constructed to perform in accordance with design specifications.

Laboratory efforts are evaluating the effects of organic chemicals and inorganic leachates on the structure and permeability (hydraulic conductivity) of compacted clay soils and comparing the results with data collected from field sites. Generally, concentrated solutions of organic and inorganic chemicals increase the permeability of clay soils and cause them to be unsuitable for controlling liquid movement in landfills. Dilute aqueous solutions of chemicals and some field leachates do not affect the permeability of clay soils, at least in short-term tests. The critical concentration at which a chemical will begin to affect soil permeability is not known for all chemicals and leachates.

Laboratory efforts are also examining: (a), the measurement and significance of effective porosity to determine if this soil property can be used in regulating soil liners; (b), the precision and bias of field and laboratory permeability (hydraulic conductivity) measurements; (c), measurement of adsorption coefficients in batch soil studies for use in designing liners to retard the movement of pollutants.

Field studies using clay soil liner test sections constructed with actual equipment and soil handling procedures are examining: (a), the ability of laboratory measurements to predict actual field permeability; (b), usefulness of procedures for predicting liquid transit time, i.e., the time for liquids such as water, leachate, etc., to move through the liner; (c), methods for optimizing construction unit operations to achieve permeability of 10^{-7} cm/sec.

Technical Resource Documents have been developed to collect and analyze information on design, construction, and evaluation of clay liners and information on use of batch adsorption procedures to design clay liners for pollutant removal. These TRD's have been published for public comment; revised versions will be published.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC has become an area of increased importance and emphasis in the design and construction of land disposal facilities. It is a critical element in the fabrication of materials, e.g., FML, drainage nets, etc., design and construction of system components, e.g., covers, clay and FML liners, drain systems, etc., and the construction of the whole facility. The design, implementation and adherence to a strong QA/QC plan are among the major factors in assuring that land disposal facilities successfully perform as they are designed to do.

This program area has been addressed indirectly in several previous projects dealing with soil liner hydraulic conductivity measurements, FML seaming and inspection requirements, subsurface preparation, liner bedding requirements, and similar activities. The first project to address this area directly was the preparation of a technical guidance document entitled, "Construction Quality Assurance for Hazardous Waste Land Disposal Facilities," EPA530/SW/85/021, which presents summaries of state-of-the-art technologies and evaluation technologies determined to constitute good engineering designs, practices, and procedures. Upon publication in late 1986, it will support the Resource Conservation and Recovery Act (RCRA) TRD's and Permit Guidance Manuals by describing current technologies and methods for designing hazardous waste facilities and for evaluating the performance of the facility design. The document discusses QA/QC requirements in foundations, dikes, low permeability soil liners, flexible membrane liners, leachate collection systems, and final cover systems.

Because QA/QC is a complex area, the research continuing in FY'87 will proceed at a deliberate and reasonable pace. HWERL will keep abreast of QA/QC activities being performed by other research organizations so as additional information becomes available on sampling requirements and factors critical in fabrication and construction of facilities it can be added to the guidance.

EXPERT SYSTEMS

The objective of this activity is to develop user friendly computer based systems that will assist the permit writer in evaluating a permit for treatment, storage and disposal facilities. These systems will emulate the decision processes of subject specialists (experts) by incorporation of their heuristic rules they use to arrive at a particular decision in their specialized area.

The research to date includes a fundamental study to determine the sequence of developing the system. Priorities for individual permit components, e.g., FML chemical compatibility, closure, waste analysis, etc. were identified.

Research is underway on FML chemical compatibility, surface impoundment evaluation, subsidence, and waste analysis. These modules should be available for testing in early 1987. The module on facility-closure and post-closure plans system have been initiated as well as construction quality assurance. These later two modules should be available for testing in 1988.

The TRD developed in this area, EPA/530-SW-84-009/10 "The Hydrologic Evaluation of Landfill Performance (HELP) Model," is being updated to incorporate the two-dimensional aspects of landfill cover systems and recently acquired field data. The field data is being used to calibrate and refine the model. Final publication of these documents is expected in late 1987.

CORRECTIVE ACTION

Corrective action is required to clean up releases from land disposal sites that have adversely affected groundwater. The applicable technologies would be similar to those in use at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites where subsurface water has been contaminated. Although described as repairs or maintenance, corrective actions are also required in other parts of the regulations. Emergency repairs of covers, liners, and leachate systems during the active life of a disposal site are required by all treatment, storage, and disposal facilities.

Corrective action will involve identifying problems at waste disposal units that cause releases to the environments and applying engineering and management methods to correct the problems. HWERL will closely follow OSW efforts to set up procedures for determining releases of pollutants form RCRA facilities, to develop guidance in setting up assessments, and to initiate needed assessments.

NON-HAZARDOUS WASTE FACILITIES

SUBTITLE "D" FACILITIES

The objectives of this activity are to characterize wastes, leachates, and air emissions from municipal solid waste (non-hazardous) processing and disposal facilities and from large-volume waste disposal facilities, and assess control methods. This research is being conducted to support legislative requirements of HSWA that the Agency review and modify, if necessary, the current criteria being used to manage non-hazardous municipal, commercial, and mining wastes (Subtitle "D").

Laboratory studies include the exploration of chemical and biological methods for rapid stabilization of municipal solid waste sites in an attempt to render them and their leachates inactive or less harmful to the environment. Recirculation, soil filters, and other methods of treatment are being investigated in conjunction with stabilization methods. Experimentation with the control of methane from municipal solid waste by lime injection is being conducted to measure the gas production rates and quantities, measure leachate volumes and composition, and compare the lime treated gas generation to previous results from untreated simulators.

Modeling efforts include the development of an improved model for predicting leachate quantity and quality and the use of previously developed models which predict gas migration to design gas controls and develop general gas control design guidance.

Current field studies are identifying the types of problems that occur at Subtitle "D" facilities, review current practices for dealing with problems, and suggest potential technologies for correcting problems. Detailed chemical analyses of liquid phases of municipal landfill gas condensate are being performed to determine if these different liquid phases have any hazardous waste characteristics. Samples are also being taken of ash residuals from actual municipal waste combustion facilities. These residuals are being analyzed to determine their levels of hazardous constituents.

TECHNOLOGY TRANSFER

TECHNICAL RESEARCH DOCUMENTS

Technology transfer encompasses the collection, documentation, and dissemination of scientific and technical information, including (a), data on the performance and costs of using the technology, (b), the transformation of research and technology into processes, products, and services that can be applied to public or private needs and (c), the secondary application of research or technology developed for a particular mission that fills a need in another environment.

The technology transfer requirement is being met with the publication of the TRD's and Handbooks, the presentation of technical seminars, and by direct technical assistance.

Assessment of a Prototype System For Pyrolysis of Refused Derived Fuel

by

Stephen Thorndyke
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for presentation at

Ontario Ministry of the Environment
Technology Transfer Conference

Sheraton Centre, Toronto
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ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL

EFW Systems Incorporated have developed and constructed a prototype unit to pyrolyse refuse derived fuel (RDF), with the intent of using the pryrolysis gases as an engine fuel to generate electricity and as a source of process heat for the pyrolyser. An assessment of the prototype unit has been made to characterize the process and compare emissions with conventional municipal solid waste (MSW) incineration techniques.

The sampling and analytical program is briefly discussed, covering sampling and analytical methodologies, process operating results, composition of the pyrolysis gas fuel and emissions in the pyrolysis gases. Data are presented to show the impact on air quality if pyrolysis gases were emitted directly to the atmosphere. An approximate energy balance for the unit shows that process modifications would be required to produce significant amounts of pyrolysis gas for use as an engine fuel.

INTRODUCTION

With increased difficulties in locating suitable landfill sites for municipal refuse disposal, alternative disposal methods are being pursued as an essential component of most waste management programs. These methods generally can be classified as either biological or thermochemical conversion. The thermochemical conversion methods are often accompanied by energy recovery and offer the advantage of greatly reducing the volume of the refuse. For example, complete combustion is often used to generate steam for industrial use, whereas partial combustion is used to produce fuels or chemical feedstock. Complete combustion facilities were initially developed many years ago and are currently in widespread use. There are some full-scale partial combustion facilities in operation but most of these processes are still in the developmental stage.

Air pollution is recognized as the potentially most serious limitation to the use of complete combustion facilities to dispose of municipal refuse. Numerous studies have identified particulate matter, acid gases, trace organics and trace metals as contaminants which may be emitted in significant amounts. However, with appropriate combustion conditions and air pollution control devices, studies have shown that emission rates of these contaminants can generally be maintained within current Ontario air emission standards and guidelines. Few studies have been carried out to investigate potential air pollution problems associated with partial combustion processes. One of these partial combustion processes is pyrolysis, and a study, sponsored by the Ontario Ministries of Energy and the Environment, was carried out to assess the performance and determine the emissions of airborne contaminants for a pyrolysis system.(1) Pyrolysis has the advantage that a fuel is produced which can be stored and transported. There may also be cost advantages over conventional municipal refuse incinerators.

PYROLYSIS PROCESS

The refuse pyrolysis process involves heating the refuse in the absence of air to a temperature of about $800^{\circ}C$ or higher.(2). The gaseous product, containing hydrogen, carbon dioxide, carbon monoxide, methane and water vapour as the major components in varying amounts, has a heating value of about 20 MJ/kg on a dry basis. This gas, usually termed a medium energy gas, requires treatment to remove impurities such as particulate matter, gaseous impurities and condensible organics before it can be used as a fuel or for other purposes.

The pyrolysis system investigated in this study is a prototype unit, built by EFW Systems Incorporated. This is a continuous moving-bed system with a nominal feed rate of 1000 kg/h, although the feed rate during the study was about 545 kg/h of shredded refuse with inorganic components removed, or refuse derived fuel (RDF), and containing about 10% moisture.

In this prototype unit, indirect propane combustion is used to initiate pyrolysis of the RDF and the pyrolysis gases are flared to the atmosphere without further treatment, as shown in Figure 1. During commercial operation, a portion of the pyrolyser gases would be directly combusted to provide heat for pyrolysis initiation and the remainder would be combusted in a spark-ignited Waukesha gas engine to generate about 350 kW of electricity.

STUDY OBJECTIVES

The overall objective in constructing and evaluating the EFW pyrolyser was to determine if this particular pyrolysis process is a viable alternative to conventional incineration for disposing of RDF.

Specific objectives of the test program carried out by ORF were as follows:

- to characterize the major gaseous components in the EFW pyrolysis gases so that the suitability of using this product as an engine fuel, after the removal of impurities, can be assessed.
- to measure the concentrations and emission rates of potential contaminants in the pyrolysis gases as a basis for an environmental assessment of the EFW pyrolysis process.
- to determine the conversion efficiency and energy efficiency of the EFW pyrolyser.

TESTING PROGRAM

On the basis of results from previous emission tests at refuse combustion facilities,(3) the following groups of potential contaminants in the pyrolysis gases were included in the present study.

- particulate matter
- acid gases
- dioxins and furans
- PCB's, chlorobenzenes and chlorophenols
- polycyclic aromatic hydrocarbons
- trace metals

Of principal concern to the study were dioxins (polychlorinated dibenzo-p-dioxins) and furans (polychlorinated dibenzofurans). Dioxins and furans in the flue gases at conventional refuse incinerator originate either from their presence in the refuse, (4) or they are formed during conventional refuse combustion from precursor compounds such as PCBs, chlorobenzenes and chlorophenols. Studies have shown that amounts of these compounds in incinerator emissions can be significant compared with the Ontario provisional guidelines, but with good combustion conditions (that is: high temperatures, good mixing and adequate residence time), emission rates can be greatly reduced. Polycyclic aromatic hydrocarbons, some of which are considered to be carcinogenic, are also generally present in the flue gases from refuse incineration. All of these trace organic compounds were considered in the emission study.

Particulate matter, acid gases, and trace metals are often emitted in significant amounts from refuse combustion, but, with appropriate air pollution control equipment, concentrations can be reduced to levels below Ontario environmental standards and guidelines. In addition to sampling the pyrolysis gases, samples of the pyrolyser ash were collected for analysis.

SAMPLING AND ANALYTICAL

Except for the gaseous components of the pyrolyser gases, pyrolysis gas sampling was carried out using modified MOE Method 5 sampling trains.(5) A conventional Method 5 train is shown in Figure 2.

A single train was used for all the trace organic compounds. In a preliminary test, an ASME(6) version of the train was used in which the flue gas sample was passed successively through a probe, particulate filter, Amberlite XAD-2 resin cartridge and impinger solutions.

This train is generally accepted as the standard method for trace chlorinated organic sampling. This test was unsuccessful, however, because organic compounds quickly condensed in the resin cartridge and restricted the sample flow. Therefore, a different train was used in succeeding tests, which consisted of a probe, particulate filter, impinger solution and Florisil adsorbent cartridge. This train was developed by the Ontario Ministry of the Environment a few years ago and has been shown to be effective for sampling trace chlorinated organics.(4)

Particulate matter, acid gases and trace metals were sampled in a single train. The flue gas sample was passed successively through a probe, particulate filter, dilute sodium hydroxide impinger to collect acid gases and some metals (antimony, arsenic, selenium and tellurium), dilute nitric acid impingers to collect most metals, and an acidified potassium permanganate solution to collect mercury.

Gaseous concentrations were determined using either gas chromatography or continuous analyser techniques. Hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and C-2 hydrocarbons were analysed by gas chromatography using a Carbosieve SII column and a thermal conductivity detector. Hydrogen sulfide was analysed by gas chromatography, combined with a flame photometric detector. Tedlar bags (polyvinyl fluoride) were used to collect samples for this analysis. Continuous analysers were used for oxygen, sulfur dioxide and nitrogen oxides analyses.

All trace organic analyses of the flue gas samples were carried out using gas chromatography/mass spectrometry techniques and procedures described in the ASME draft method for chlorinated organics sampling.

Most of the trace metal analyses were done by d.c. plasma atomic emission spectroscopy. Solutions were analysed directly, whereas particulate samples were digested with nitric acid and aqua regia before analysis. Silver was analysed by flame atomic absorption spectrophotometry and mercury by cold vapour atomic absorption spectrophotometry. Arsenic, antimony, selenium and tellurium were analysed by hydride generation atomic absorption.

Acid gases were analysed by ion chromatography. Cyanide was determined by a colorimetric method and ammonia was determined by reaction with Nesslar reagent.

Ultimate analyses were carried out on both the pyrolyser ash and the pyrolyser gas particulate matter.

Three separate tests were completed and average results from these tests were used to assess the pyrolyser performance.

RESULTS

Average major gaseous component concentrations in the pyrolyser gases are presented in Table 1. Hydrogen predominates with lesser amounts of methane, carbon monoxide and carbon dioxide. Other identified components are present in minor amounts. Unidentified components are believed to include residual moisture, hydrocarbons and acid gases.

In Table 2, the concentrations of the contaminants identified in the flue gases are identified. To determine the relative importance of these contaminants, the concentrations are compared with the Ontario Regulation 308 maximum permitted point-of-impingement concentrations(7) (8) as ratios of the flue gas concentration to the impingement concentration. These ratios essentially indicate how much the flue gases must be diluted to bring the impingement concentrations within the regulations, but are used in this study to indicate which contaminants are of most concern.

The highest ratio is for particulate material. However, it is anticipated that almost all of the particulate material would be removed in a scrubbing device before using the gases as a fuel. Of the gases and acid gases, hydrogen sulfide and carbon monoxide have the highest ratios. The carbon monoxide would be converted to carbon dioxide and the hydrogen sulfide to sulfur dioxide during utilization of the pyrolysis gases.

The highest metal ratio is for lead. Although no detectable amounts of beryllium were observed in any of the samples, the relatively high detection limit and very stringent emission regulation results in a high concentration ratio. From the proportions of the metals retained on the particulate filter during sampling, it is apparent that almost all the metals could be removed by scrubbing. An exception may be mercury because 98% appeared to be present as a vapour, consistent with its known high volatility.

In Table 3, emission factors for the pryolyser are compared with emission factors for MSW incineration from a recent study at a modern, efficient two-stage modular incinerator. As expected, the particulate emission factor is much higher for pyrolysis. Lower emission factors during pyrolysis occurred for hydrogen chloride and, in particular, dioxins and furans. For dioxins and furans, the lack of oxygen in the pyrolyser may be responsible for the low emission factors. Because of the very low levels present, emission factors for the dioxins and furans are essentially based upon the detection limits of the sampling and analytical methods. A very much higher emission factor was obtained for PAHs with pyrolysis.

Ultimate analyses for the fly ash and pyrolyser ash, Table 4, show high carbon analyses indicating conversion of carbon to carbon monoxide and carbon dioxide during pyrolysis was not very efficient.

Table 5 represents a material balance for the major elemental components of the refuse derived fuel, carbon, hydrogen and oxygen, during pyrolysis. Input values are based on typical values for refuse derived fuel,(9) combined with experimentally determined moisture contents. The data indicate 29% of the carbon and 51% of the hydrogen in the dry feed are converted into dry pyrolysis gases.

Table 6 summarises the composition of the dry pyrolyser product gas after treatment to remove all impurities. The higher heating value is 15.0 MJ/Nm^3 (400 Btu/scf) or 21.3 MJ/kg (9,200 Btu/lb). The dry pyrolysis gases represent about 28% of the original RDF feed material and the total pyrolysis gases, including water vapour, represent about 53% of the original RDF feed material.

An approximate energy balance, Table 7, indicates energy recovery in the pyrolysis gases is only 37%. A more favorable energy balance could be obtained by improved burnout of the refuse derived fuel, a reduction in equipment heat losses and recovery of energy during cooling of the grate ash, pyroloysis gases or combustion gases.

DISCUSSION

Results of the ORF study have shown that, under the conditions prevailing during sampling of a prototype unit, the EFW pyrolyser produces raw pyrolysis gases which contain high particulate and gaseous impurity concentrations, 141 g/m^3 and 12.8% by volume on a dry basis, respectively, in addition to a high moisture content of 40.7% by volume.

In commercial use, it is anticipated that a portion of the pyrolysis gases would be combusted to provide process heat for sustaining pyrolysis, and the remainder would be used as an engine fuel to generate electricity. Because of the presence of moisture, particulate and gaseous impurities, treatment of the raw pyrolysis gases will be necessary before use as a fuel. Without treatment, excessive contaminant emissions to the atmosphere and damage to the engine likely would result.

If all the moisture and impurities are removed during the pyrolysis gas treatment, a medium energy fuel of the following composition would result: 41% hydrogen, 21% carbon monoxide, 22% methane and 17% carbon dioxide by volume. Additional treatment may be necessary to increase the higher heating value, or to adjust the octane rating before it can be used as an engine fuel.

A comparison of potential contaminant concentrations in the raw pyrolysis gases with the maximum point-of-impingement concentrations permitted by the standards and guidelines in Regulation 308 of the Ontario Environmental Protection Act indicate that the contaminants of most concern (those with the highest required diluting ratios) were particulate matter, carbon monoxide, hydrogen sulfide, beryllium, lead and sulfuric acid. These contaminants may cause the standards and guidelines to be exceeded if the raw pyrolysis gases were emitted directly to the atmosphere without dilution. Although there are no standards or guidelines for PAH compounds, the substantial amounts of these compounds present may pose a more serious threat to the environment than any of the other potential contaminants.

With adequate flue gas control for particulate matter and acid gases, the potential threat to the environment by the pyrolysis gas contaminants would be greatly reduced. After combustion of the pyrolysis gases, either to provide process heat or as an engine fuel, it appears the regulated contaminants of most concern will be mercury, particulate matter, sulfur dioxide and perhaps beryllium. Concentrations would be low, however, and it appears that only a relatively short stack would be required for adequate dispersion of the combustion gases. Most of the metals and PAH compounds would be removed during particulate control since they are generally associated with particulate material. The amount of PAH remaining in the combustion gases will depend very much on the temperature and residence time during combustion.

Compared with the disposal of MSW in a modern two-stage incinerator, the raw EFW pyrolyser gases exhibit much higher emission factors for PAH compounds, carbon monoxide and particulate matter. An important feature of the pyrolysis gas composition is the virtual absence of trace chlorinated organics, particularly dioxin and furan compounds, together with their known precursors during combustion. Also, amounts of hydrogen chloride may be much lower with pyrolysis.

To summarize, the following conditions would have to be met to avoid adverse environmental effects from the EFW pyrolyser:

- the raw pyrolysis gases are toxic and must not be released directly to either the atmosphere or the work place.
- a high efficiency control system is required to remove most of the particulate and acid gas contaminants from the raw pyrolysis gases before use as a fuel.
- combustion of the cleaned pyrolysis gases must involve sufficiently high temperatures and long residence time to destroy the remaining PAH compounds.

From material balance calculations, the reduction in dry weight of the RDF during pyrolysis will be approximately 56%, and the conversion of carbon into gases, particulate carbon (pyrolysis gas particulate matter) or condensible compounds will be 46%. Theoretically, the weight reduction could be as high as 91% if no organic carbon or hydrogen remain in the ash, and this is the weight reduction which might be expected with conventional MSW incineration. However, maximizing the weight reduction is not necessarily the most important criterion in judging the performance of the pyrolyser, since the cost of any attempts to increase the weight reduction, such as higher process temperatures or increased solids residence time, must be weighted against reduced costs for landfill requirements.

An approximate energy balance indicates that only 25% of the energy in the refuse derived fuel is recovered in the cleaned pyrolysis gases, and this energy would be mostly required to initiate pyrolysis, with little, if any, available for electricity generation.

This situation may be overcome to some extent by improving the conversion of carbon in the grate ash and particulate emission, recovery of sensible heat in the pyrolyser and combustion gases and reducing equipment heat loses.

Thus, it is concluded that the prototype EFW pyrolyser emits significant quantities of some environmental contaminants and has an unfavourable energy balance. However, it may be possible to overcome these problems in a commercial unit, provided that it is economical to install adequate pollution control and energy recovery equipment.

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FIGURE 1

Simplified Diagram of the EFW Pyrolyser

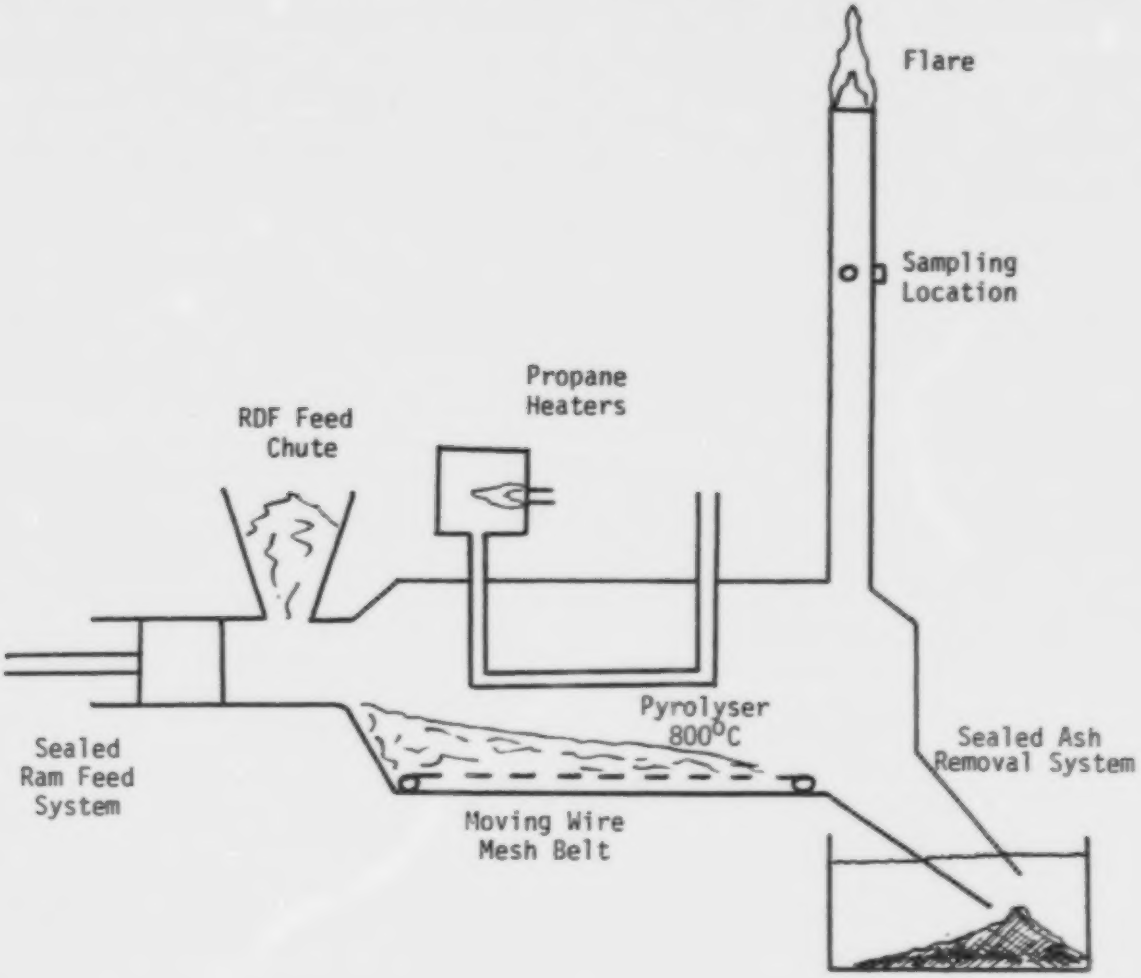
Flare
Sampling Location
Propane Heaters
RDF Feed Chute
Pyrolyser 800°C
Sealed Ash Removal System
Sealed Ram Feed System
Moving Wire Mesh Belt

FIGURE 2

Refuse Pyrolysis Emissions

Method 5 Sampling Train

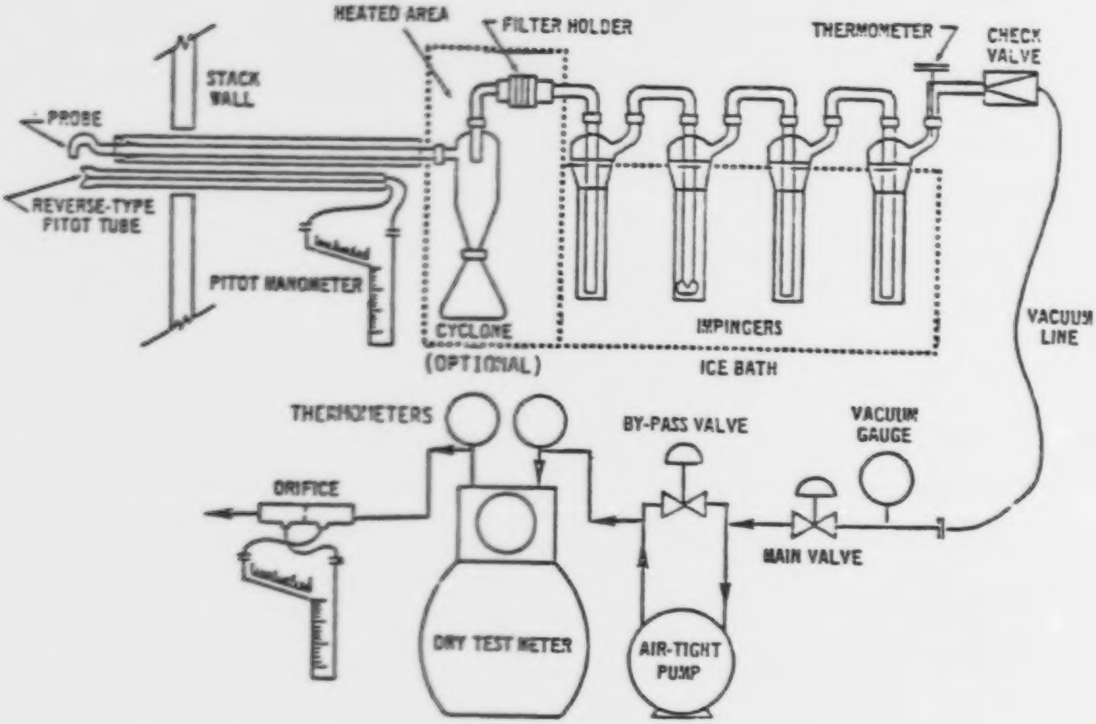
HEATED AREA
FILTER HOLDER
THERMOMETER
CHECK VALVE
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
CYCLONE (OPTIONAL)
IMPINGERS
ICE BATH
VACUUM LINE
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

TABLE 1

Refuse Pyrolysis Emissions

Average Dry Gaseous Component Concentrations

Gas	Average Concentration %
Hydrogen	35.56
Methane	19.09
Carbon Monoxide	17.85
Carbon Dioxide	14.66
C2 - Hydrocarbons	1.42
Nitrogen	0.88
Ammonia	0.35
Oxygen	0.19
Hydrogen Sulfide	0.11
Hydrogen Cyanide	0.10
Sulphur Dioxide	0.03
Other*	9.76
Total:	100.0

*Including Residual Moisture, Hydrocarbons and Acid Gases.

TABLE 2

Refuse Pyrolysis Emissions

Comparison of Flue Gas Emissions with Environmental Protection Act Regulation 308 Standards

Contaminant	Flue Gas Concentration	Maximum Impingement Concentration	Concentration Ratio
Particulate	141 g/Nm^3	100 $\mu g/m^3$	1410000
NH_3	2.5 g/Nm^3	3600 $\mu g/m^3$	686
CO	205 g/Nm^3	6000 $\mu g/m^3$	34083
HCN	1.1 g/Nm^3	1150 $\mu g/m^3$	946
H_2S	1.5 g/Nm^3	30 $\mu g/m^3$	50000
NO_2	0.02 g/Nm^3	500 $\mu g/m^3$	40
SO_2	0.65 g/Nm^3	830 $\mu g/m^3$	783
HCL	8.2 mg/Nm^3	100 $\mu g/m^3$	82
HF	0.54 mg/Nm^3	4.3 $\mu g/m^3$	126
HNO_3	4.1 mg/Nm^3	100 $\mu g/m^3$	41
H_3PO_4	2.7 mg/Nm^3	100 $\mu g/m^3$	27
H_2SO_4	202 mg/Nm^3	100 $\mu g/m^3$	2017
Sb	7.4 mg/Nm^3	75 $\mu g/m^3$	99
As	0.6 mg/Nm^3	15 $\mu g/m^3$	40
Be	0.2 mg/Nm^3	0.03 $\mu g/m^3$	6667
B	30 mg/Nm^3	100 $\mu g/m^3$	300
Cd	2.4 mg/Nm^3	5 $\mu g/m^3$	480
Cr	1.4 mg/Nm^3	5 $\mu g/m^3$	280
Cu	5.5 mg/Nm^3	100 $\mu g/m^3$	55
Pb	26 mg/Nm^3	10 $\mu g/m^3$	2600
Mn	20 mg/Nm^3	100 $\mu g/m^3$	200
Hg	2.1 mg/Nm^3	5 $\mu g/m^3$	420
Ni	2.9 mg/Nm^3	5 $\mu g/m^3$	580
Se	0.1 mg/Nm^3	20 $\mu g/m^3$	5
Ag	0.2 mg/Nm^3	3 $\mu g/m^3$	67
Te	0.1 mg/Nm^3	30 $\mu g/m^3$	3
Sn	2.2 mg/Nm^3	30 $\mu g/m^3$	73
V	0.9 mg/Nm^3	5 $\mu g/m^3$	180
Zn	23 mg/Nm^3	100 $\mu g/m^3$	230
PCDD + PCDF	19 ng/Nm^3	450 pg/m^3	42
PCBs	13 $\mu g/Nm^3$	450 ng/m^3	29

TABLE 3

Refuse Pyrolysis Emissions

Comparison of Refuse Pyrolysis and Combustion Emissions

Contaminant	Emission Factor Units	RDF Pryolysis Emission Factors*	MSW Incineration Emission Factors*
Particulate	g/kg	75.4	1.3
Hydrogen Chloride	mg/kg	4.3	6770
Antimony	mg/kg	3.9	3.5
Cadmium	mg/kg	1.3	5.9
Chromium	mg/kg	0.8	0.3
Lead	mg/kg	13.7	84.0
Mercury	mg/kg	1.1	4.3
Nickel	mg/kg	1.5	1.5
Dioxins	ng/kg	9.5	658
Furans	ng/kg	6.5	877
PCBs	µg/kg	6.7	5.3
PAHs	mg/kg	1100	0.05

*Dry Basis

TABLE 4

Refuse Pyrolysis Emissions
Ultimate Analysis of the Pyrolyser Ash

	Dry Analysis, % By Weight	
	Fly Ash	Pyrolyser Ash
Carbon	92.5	44.1
Hydrogen	2.0	1.5
Ash*	5.5	43.9
Nitrogen	-	1.1
Chlorine	-	0.4
Sulfur	-	0.5
Oxygen	-	8.5

* By Difference

TABLE 5

Refuse Pyrolysis Emissions

Elemental Material Balance

	Carbon g/s	Hydrogen g/s	Oxygen g/s
Input			
Refuse	61.74	8.22	50.95
Moisture		1.64	13.09
Output			
Hydrogen		2.04	
Carbon Monoxide	6.14		8.18
Methane	6.56	2.19	
Carbon Dioxide	5.04		13.44
Oxygen			0.17
Moisture		3.77	30.13
Flue Gas Particulate	9.55	0.19	
Grate Ash*	34.45	1.35	12.12
Total Input/Output	61.74	9.86	64.04

* By Difference

TABLE 6

Refuse Pyrolysis Emissions

Properties of the Dry Gaseous Product

Component	Composition	
Hydrogen	40.8% vol.	4.8% wt.
Carbon Monoxide	20.5% vol.	32.8% wt.
Methane	21.9% vol.	20.3% wt.
Carbon Dioxide	16.8% vol.	42.1% wt.
Total:	100.0% vol.	100.0% wt.
	Emission Rate	Emission Factors
Hydrogen	2.0 g/s	0.013 g/g
Carbon Monoxide	14.0 g/s	0.092 g/g
Methane	8.5 g/s	0.056 g/g
Carbon Dioxide	18.0 g/s	0.119 g/g
Total:	42.5 g/s	0.281 g/g
Higher Heating Value	15.03 MJ/Nm^3 (400 Btu/scf)	21.33 MJ/kg (9,200 Btu/lb)

TABLE 7

Refuse Pyrolysis Emissions Approximate Energy Balance

Energy Input

RDF Heat Content = 2.48 MW
Propane Heat Content = 1.13 MW

Total = 3.61 MW

Energy Output

Pyrolysis Gas Heat Content = 0.91 MW

Pyrolysis Gas Sensible Heat = 0.25 MW

Grate Ash Heat Content = 0.34 MW

Fly Ash Heat Content = 0.35 MW

Propane Combustion Gas Sensible Heat = 0.61 MW

Miscellaneous* = 1.15 MW

Total = 3.61 MW

* Including grate ash sensible heat, equipment heat losses and heat content of unidentified pyrolysis gas components.

MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC

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MUNICIPAL SOLID WASTE
FEASIBILITY OF GASIFICATION WITH PLASMA ARC

Presented to
1986 Technology Transfer Conference
December 8, 1986

BACKGROUND

Resorption Canada Limited (RCL) is a private high tech firm which was federally incorporated to design, fabricate, market and service industrial systems utilizing plasma arc technology. The Company is heavily R&D oriented since this technology is still relatively new to the Canadian industrial marketplace. Plasma arc has potential wide applicability in business and industry where a controlled source of intense heat is required.

RCL operates a plasma research facility in Ottawa, Ontario in which it conducts tests, research experiments and demonstrations utilizing a specially designed 150KW plasma arc torch. A plasma arc torch is a device for producing an electrical "flame" called a plasma which is the hottest, sustainable flame known to man. The plasma arc torch takes a very small quantity of any gas (argon, hydrogen, helium, nitrogen, oxygen, air, etc) and, using electricity, changes this gas into a plasma flame. Unlike a combustion burner flame the plasma flame can be generated in the total absence of oxygen. Heat is, therefore, generated by electrical dissociation and ionization of the gas, which can be extensively exploited in many heating applications. The arc centreline temperature can be in excess of 10,000 deg C and the arc edge temperatures can be between 3,000 and 8,000 deg C. The torch is designed and built with no moving parts for trouble free performance and easy maintenance, and it can have an electrical to thermal conversion efficiency of over 90% depending on the size of the torch. When the plasma arc torch is operated as a self contained Plasma Heating System in a reactor vessel with the exclusion of oxygen the resultant processing of input materiel approaches pure pyrolysis.

Over the years a wealth of experience and knowledge has been gained with the plasma arc torch as the heat source for the processing of a wide range of input materiels. A major area of concentration has been in the processing of carbonaceous materiel in which pyrolysis provides for virtual complete gasification of all combustibles in the source materiel, while non combustibles are reduced to a virtually inert slag. The high process temperatures achieved by plasma processing ensure rapid and complete breakdown of chemical bonds and avoid the particulates and partially combusted hydrocarbons normally associated with combustion processes. Total gasification can, therefore, be achieved very efficiently. The general absence of oxygen results in significantly less air pollution from contaminants such as nitrous oxides (NOx) and sulphur dioxide (SO2) than is associated with conventional gasification processes.

The plasma arc processing of Municipal Solid Waste (MSW), with its high carbonaceous content, combines energy production with the destruction of a waste materiel with what is considered to be minimal environmental pollution. The characteristics of MSW gasification were developed a number of years ago through R&D work performed at the facilities of Plasma Energy Corporation (PEC) of Raleigh, North Carolina, with whom RCL has always been closely affiliated. The postulated 4-5 fold increase in usable output energy compared to input electrical energy represents a theoretical recovery of approximately 95% of the available energy in the input materiel, which together with the potential 300-350 BTU/scf product gas, the potential 20 to 1 volume reduction ratio of the silica metallic slag compared to the input MSW and the potential minimal requirement for environmental controls are very attractive process characteristics. This becomes even more attractive when considered with the design simplicity, low capital costs and operating versatility of a plasma arc gasification installation. However, prospective clients view these results as inconclusive since they were neither performed nor published in Canada, and there is no operational system in either Canada or the US which utilizes this technology in this application.

FEASIBILITY STUDY PROPOSAL

In an endeavour to authenticate these postulated characteristics and to increase the visibility and potential acceptability of the use of plasma technology in the gasification of MSW, RCL together with OBOE Engineering Limited of Ottawa and Ontario Hydro Research Division submitted an unsolicited proposal to the Ontario Ministry of Energy for consideration for funding of a feasibility study. The study was to be conducted in two stages, Stage 1 to determine the higher heating value of the product gas and the total process energy balance, and Stage 2 to determine the environmental acceptability of the process and the subsequent combustion of the product gas.

Stage 1 would concentrate on the determination of:

- the electrical power required to process a unit of input MSW;
- the volume of product gas generated from a unit of MSW input;
- the higher heating value (HHV) of the product gas compared to the HHV of the input MSW;
- the process heat losses;
- the potential commercial application for the output slag;
- the chemical composition of the output slag;
- the volume and weight ratios of output slag compared to input MSW; and

- the potential enthalpy of the product gas.

And then Stage 2 would concentrate on:
- analysis of the product gas for pollutants;
- analysis of the condensate extracted through drying of the product gas;
- analysis of the products of combustion of the product gas; and
- analysis of the resultant slag for pollutants.

Stage 1 was approved for a 1 April 1986 commencement with 52% of the estimated $252K cost being funded by the Ministries of Energy and Environment. The remainder of the Stage 1 funding will to be provided by the participants of the project and by Plasma Energy Corporation. Stage 2 will be reassessed for funding approval depending on the results obtained through Stage 1. The estimated cost of Stage 2 is $170K.

All experimental work is being performed in the RCL plasma research facility. The original facility, as depicted in Figure 1, required certain modifications in order for the required operational characteristics of such a process to be most accurately determined. The modified facility is depicted in Figure 2. Paramount among the changes were:
- the fabrication of a new reactor vessel complete with a hydraulic assisted feed system to better match the size of the existing plasma arc torch and to permit continuous feed throughout the full period of an experimental run;
- the addition of a condenser to dry the product gas to determine its maximum heating value;
- the addition of a blower system in the product gas line to draw the product gas to alleviate back pressure in the reactor vessel and hence alleviate materiel feed difficulties;
- the modification of the product gas cooler from a

bubble process to a spray process to improve the efficiency of the blower system; and
- the addition of a Gas Chromatograph to permit immediate readouts of the chemical composition of the product gas to ensure maximum accuracy.

Stage 2 will also require further modifications to the facility, however, only to the extent of providing a capability to store the product gas for later use in an extended combustion test. The combustion of this gas will be conducted in the existing boiler in the RCL plasma research facility.

THE EXPERIMENTAL PROCEDURE

MSW throughput in the 150KW plasma arc facility is estimated at 400-500 pounds per hour. Each experimental run will cover an eight hour period, therefore, upwards of two tons of MSW will be required per run. This MSW will be shredded, if shredded city refuse can be readily found, however, the facility could also accommodate "as received" city refuse provided no large objects are present. Standard garbage bags from residential streets could be handled very easily. The use of shredded garbage could more easily and probably more accurately permit ultimate and proximate analyses for comparison purposes. Steam can be introduced, as required, and at varying rates to provide additional free hydrogen to aid the process.

The control system is very versatile and enables one operator to process varying amounts of materiel from next to nothing to the maximum capability of the facility depending on the type of materiel being processed. The operator has continuous readout of:
- torch position within the reactor vessel;
- torch operating current and voltage;
- torch air input temperature and flow rate;

- torch coolant water input/output temperatures and flow rate;
- input materiel feed rate;
- process temperature within the reactor vessel;
- gas cooler/condenser input/output gas temperatures;
- gas cooler water input/output temperatures and flow rate; and
- reactor vessel pressure.

If certain of these parameters exceeds preset tolerance levels, the torch is automatically interlocked off.

The process temperature, as monitored at the inside wall of the reactor vessel, will be approximately 2000 deg F although varying temperatures will be tried in an endeavour to find the optimal temperature. The vessel will be preheated to this temperature prior to any processing being done. This preheating will be achieved through the use of a natural gas burner for the first 500 deg C, approximately, and then through the use of the plasma torch for the remainder.

Once the operating temperature is achieved, processing can commence. MSW will be weighed and then fed into the feed hopper. The feed hopper has two doors, one at the top and one between the hopper and the reactor vessel. The hopper will be filled with the inside door closed to retain heat in the vessel and to prevent the massive insertion of air. Once the hopper is full, the top door will be closed and the inside one will be opened to permit the MSW to be hydraulically fed into the vessel. The hydraulic system is adjustable to permit a variable rate of input materiel to be fed into the vessel. A plunger is also available to guard against blockages. The input materiels handler will maintain a specified level of MSW in the hopper to guard against the ingestion of large amounts of air into the process. With this specified level being maintained, the inside door can be left open for the full duration of the test. The pyrolysis operator will monitor the processing rate through the temperature sensor in the top of the vessel. An increasing temperature will indicate that the vessel is emptying and a lowering temperature will indicate that the MSW is being fed too rapidly. A sight window is also available so that the materiel level can be visually checked whenever needed. The Pyrolysis Operator will establish the optimum feed rate for the process. Varying the torch input power will cause a corresponding variation in the optimum feed rate.

Output slag will be permitted to accumulate in the bottom of the reactor vessel and will be removed through a trap door by hydraulically tipping the entire vessel. At a 20 to 1 volume reduction ratio between the input materiel and the output slag it is anticipated that a full experimental run can be conducted without the need for slag output. The slag will then be removed from the vessel at the end of each run in preparation for the next run.

The volume of product gas generated will be continuously recorded on a Bailey gas meter, which will be calibrated prior to the commencement of any experimentation, and a continuous log of all torch operating parameters will be maintained to facilitate full analyses at a later time. All other power usages through the process will also be monitored together with all process temperatures to facilitate the determination of heat transfer rates and the process heat balance. The product gas chemical composition will be monitored on a periodic basis to ensure a good cross sectional reading of the product gas quality. The product gas will be flared on exit since no further use of it will be required through Stage 1. The intent through the study will be to vary the operational parameters and monitor the resultant performance characteristics to determine the best operating characteristics. Figure 3 depicts the process energy balance considered achievable as derived from R&D conducted to date.

PRELIMINARY TESTING

Immediately preceeding the commencement of this feasibility study RCL conducted preliminary experimentation in the gasification of MSW for Plasma Energy Corporation. These tests were conducted in the original unmodified facility, therefore, obvious inefficiencies were present. Preliminary environmental analyses of the product gas was also conducted, as was preliminary chemical analyses of the resultant slag. The results obtained, although inconclusive due primarily to the lack of quantity of tests performed, indicated the feasibilty of the process and the potential achievability of the postulated characteristics. The analyses of the resultant slag, for example, strongly supported the claim that the slag is inert and non-leachable. This level of testing, however brief, proved very beneficial at the commencement of the current feasibility study in the determination of initial process parameters.

CURRENT STUDY STATUS

We are currently approximately two thirds of the way through Stage 1. We have effected all modifications to the facility and are now commencing operational testing. Nine operational tests are scheduled, after which the results will be fully analysed and a Stage 1 report will be prepared. It is anticipated that Stage 1 will be complete by approximately 1 March 1987. The results portrayed in the Stage 1 report will form the basis of a decision by the Ministries of Energy and Environment on whether or not to consider funding support for Stage 2.

BENEFITS/ADVANTAGES

The disposal of MSW is becoming an ever increasing problem for municipalities and environmental protection agencies alike. The standard age old disposal method of landfill is becoming increasingly less attractive as such sites are becoming full, alternate sites are becoming scarce and the knowledge and reality of contamination of adjacent facilities and property is becoming more prevalent and frightening. The alternative to landfill for MSW disposal has primarily been incineration in a number of forms. However, these forms of disposal have not been without their problems, from environmental to general public rejection on aesthetic grounds.

The success of this feasibility study to prove the postulated parameters of operation of plasma arc for the gasification of MSW could be extremely beneficial for this application, coming at a time when new and more environmentally acceptable solutions are sorely needed. This would not only open up a complete new application field for this emerging technology but it could be a significant boon to an ever increasing number of municipalities with existing city refuse problems. This would not merely be another way to get rid of MSW, but it could be a technological breakthrough with significant benefits.

The major benefits/advantages from this process could be:

- the standard output product of the plasma arc process is a producer gas which offers considerably more flexibility for use than, for example, sites which only produce steam;
- plasma arc gasifiers can have substantially lower capital costs since they can integrate more fully into a potential owner's existing facility, as compared to sites which require integral steam boilers thereby increasing the cost of these sites by 25 to 30%;
- the output energy of the plasma arc gasifier, being a producer gas, can be stored for future use similar to natural gas, as compared to steam boiler installations where the energy is lost if it is not used virtually immediately;
- the operating temperature and the heat transfer rate of

the plasma arc process can be variable, relatively at will, therefore, the optimum operating temperature and rate of reaction can be achieved, varied and maintained to minimize undesirable output pollution products and maximize the energy recovered from the input materiel;

- the plasma arc gasification process does not depend on the combustion of any of the input materiel for the pyrolysis process, therefore, the quantity of output energy produced per unit of input materiel can be maximized;
- plasma torches have the potential to deliver the heat of reaction much faster than conventional heat sources enabling the complete breakdown of the input materiel and the production of smaller molecules which are inherently less hazardous;
- the ability to process materiel at any rate from next to nothing up to the maximum capacity of the facility and still operate at the optimal operating point is a very desirable feature;
- the fact that the materiel enters into two chemical reactions, once during the pyrolysis process for the generation of the product gas, and once during the product gas combustion process, before any by-products are exhausted to the atmosphere ensures minimization of pollutants;
- metallics and glass in the input materiel melt, thus substantially reducing the volume of the output slag and alleviating problems with its disposal; and
- there is a potential commercial market for the slag produced through plasma arc gasification of MSW thereby virtually eliminating the requirement for continued operation of controlled landfill sites for MSW.

DISADVANTAGE

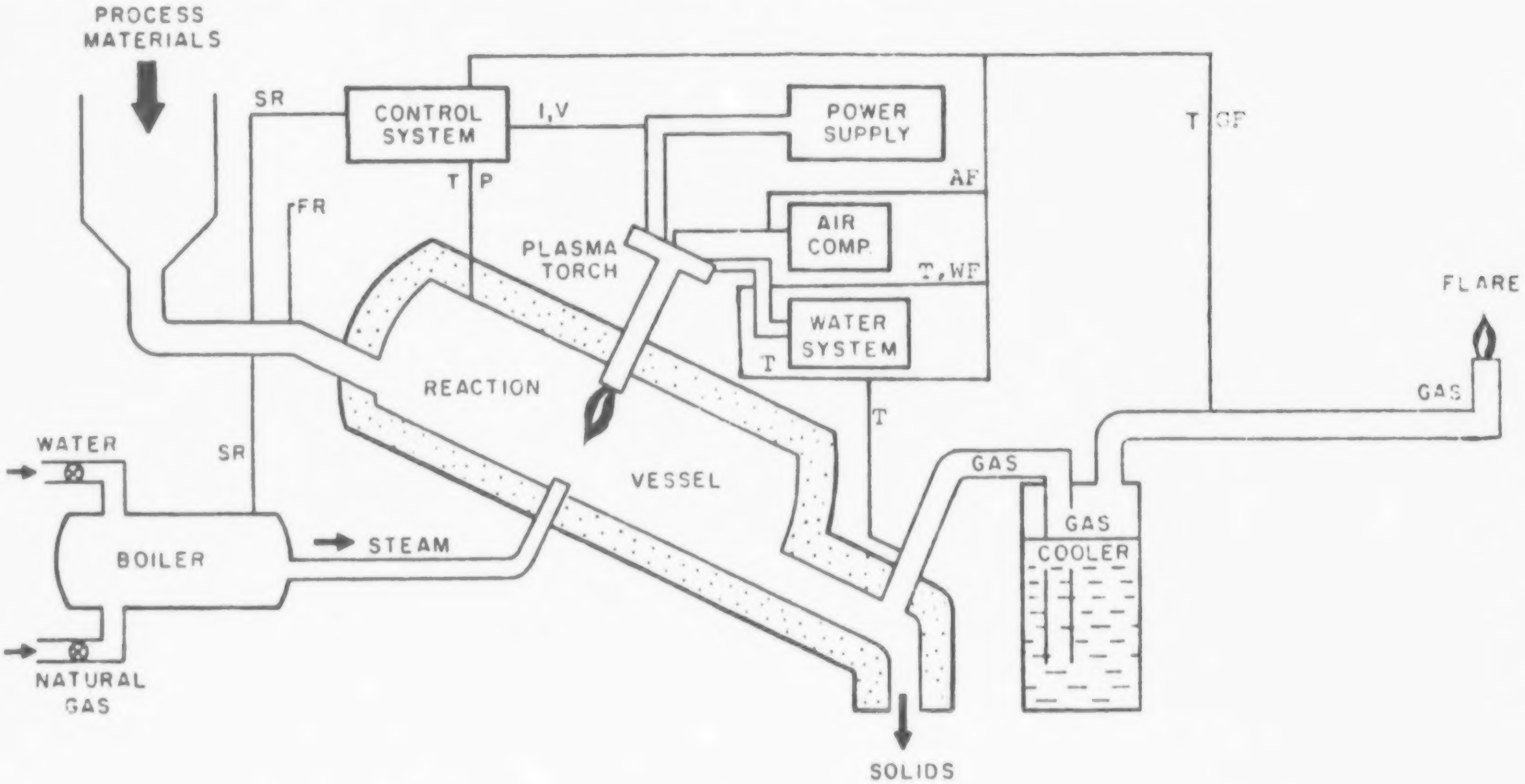
The primary disadvantage in this process is the operating costs associated with the high electrical consumption. This cost is somewhat offset by the higher volume of product gas generated and, in some cases, it can be further alleviated by operation at lower power during peak hydro usage periods. For example, demand charges can be from 30%-90% lower, depending on the hydro district, for operation between 8PM and 8AM and all day Saturday and Sunday, which potentially can be used to advantage. The extent of this advantage would be dependent on the design and operational characteristics required of the installation.

CONCLUSION

The participants in this feasibility study remain very optimistic that the experimentation will be highly successful and the plasma gasification of Municipal Solid Waste will become a fact of the future.

RESORPTION
CANADA LIMITED

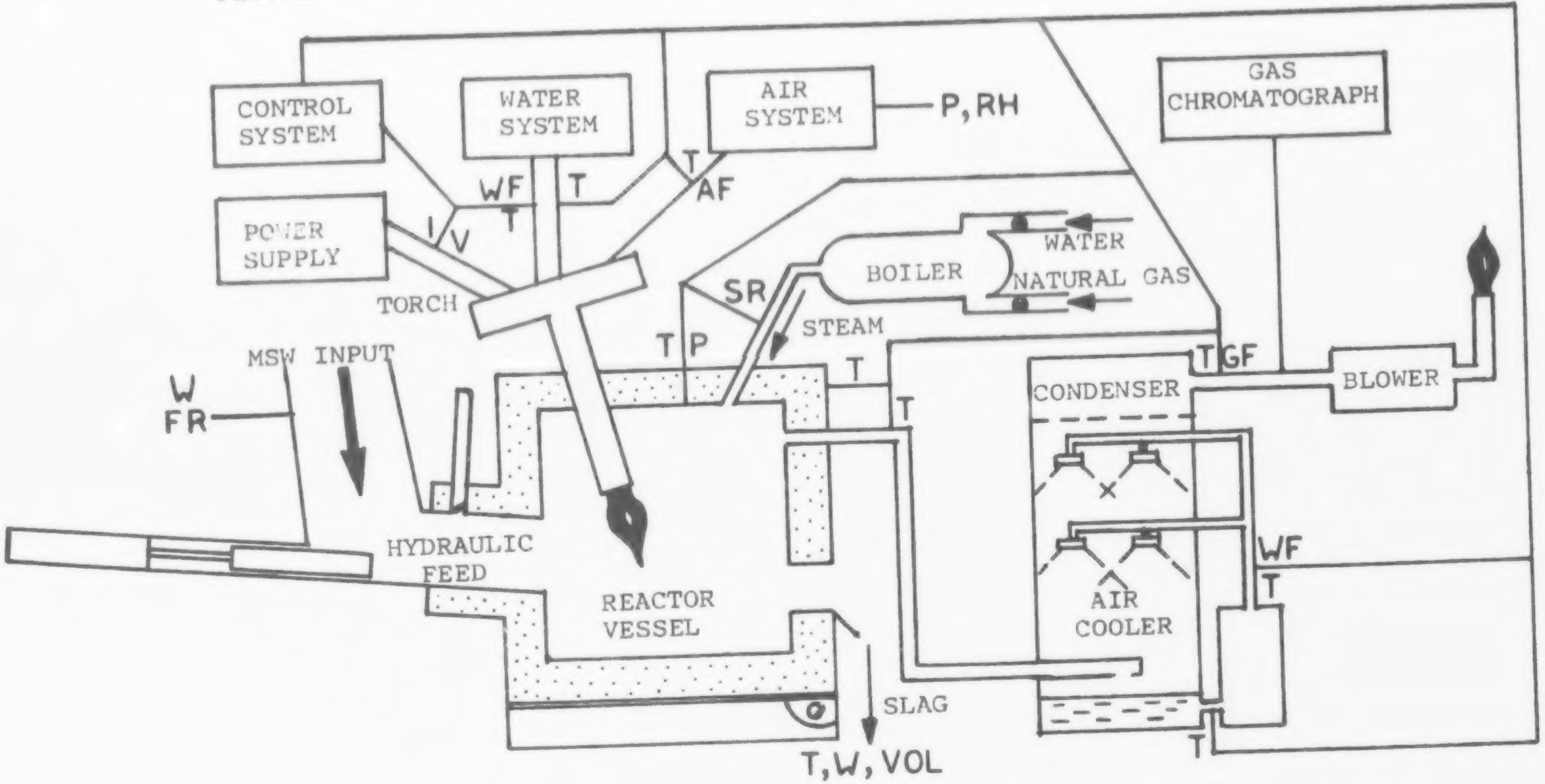
FIGURE 1 - PLASMA RESEARCH FACILITY - ORIGINAL


PROCESS MATERIALS
SR
CONTROL SYSTEM
I,V
POWER SUPPLY
T GF
T P
FR
AF
AIR COMP.
PLASMA TORCH
T,WF
WATER SYSTEM
T
FLARE
REACTION
T
GAS
WATER
SR
GAS
VESSEL
GAS
BOILER
STEAM
COOLER
NATURAL GAS
SOLIDS

I - CURRENT (AMPS)   V - VOLTAGE (V)   T - TEMPERATURE (DEGREES C)
FR - MAT'L FEED RATE (LBS/HR)   SR - STEAM RATE (LBS/HR)   P - PRESSURE (PSIG)
AF - AIR FLOW RATE (CFM)   WF - WATER FLOW RATE (GPM)   GF - PRODUCT GAS FLOW RATE (SCFH)

RESORPTION
CANADA LIMITED

FIGURE 2 - PLASMA RESEARCH FACILITY - MODIFIED

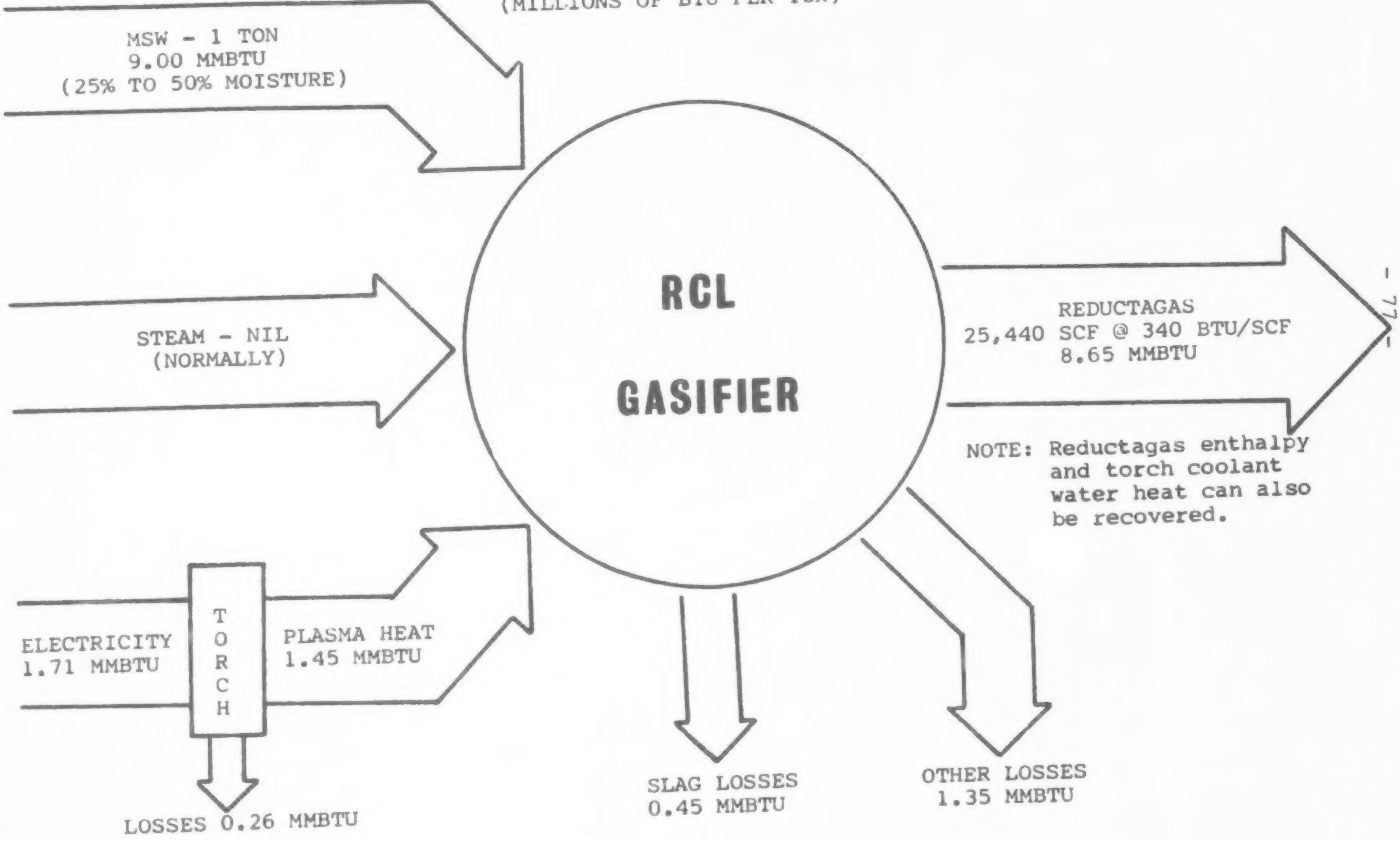

CONTROL SYSTEM
WATER SYSTEM
AIR SYSTEM
P, RH
GAS CHROMATOGRAPH
POWER SUPPLY
WF
T
I
V
T
T
AF
TORCH
SR
BOILER
WATER
NATURAL GAS
STEAM
T
P
T
T
TGF
BLOWER
CONDENSER
W
FR
MSW INPUT
HYDRAULIC FEED
REACTOR VESSEL
AIR COOLER
WF
T
SLAG
T
T, W, VOL

I - CURRENT (AMPS)
V - VOLTAGE (VOLTS)
T - TEMPERATURE (DEGREES C)
FR - MAT'L FEED RATE (LBS/HR)
SR - STEAM RATE (LBS/HR)
P - PRESSURE (PSIG)
AF - AIR FLOW RATE (CFM)
WF - WATER FLOW RATE (GPM)
GF - GAS FLOW RATE (SCFH)
RH - RELATIVE HUMIDITY (%)
W - WEIGHT (LBS)
VOL - VOLUME (CF)

FIGURE 3 - RESORPTION CANADA LIMITED

MUNICIPAL SOLID WASTE GASIFICATION YIELDS

RESEARCH AND DEVELOPMENT RESULTS
(MILLIONS OF BTU PER TON)


MSW - 1 TON
9.00 MMBTU
(25% TO 50% MOISTURE)
STEAM - NIL
(NORMALLY)
ELECTRICITY
1.71 MMBTU
TORCH
PLASMA HEAT
1.45 MMBTU
LOSSES 0.26 MMBTU
RCL
GASIFIER
REDUCTAGAS
25,440 SCF @ 340 BTU/SCF
8.65 MMBTU
SLAG LOSSES
0.45 MMBTU
OTHER LOSSES
1.35 MMBTU

NOTE: Reductagas enthalpy and torch coolant water heat can also be recovered.

SEWAGE SLUDGE COMPOST AS TURF FERTILIZER

J.L. Eggens, N.L. Pierce, and C.P.M. Wright

University of Guelph
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SEWAGE SLUDGE COMPOST AS TURF FERTILIZER

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Abstract. The suitability of the Windsor composted sludge for turf was evaluated on home lawn-type turf (primarily *Poa pratensis* L.) at the Horticultural Research Station at Cambridge and on mixed *Poa annua* L. and *Agrostis palustris* Huds. turf at the Weston Golf and Country Club, Weston, Ontario. At both locations, turf fertilized with the Windsor material was as similar to turf fertilized with urea. At the Cambridge site, the turf treated with the Windsor material (+urea) was similar to that treated with Milorganite. There appeared to be no difference in thatching tendency, susceptibility to drought or disease, in turf color or turf growth. On the golf course turf, the speckling commonly noted with urea was not evident with the Windsor material. A *Poa annua* L. sward has been established at the Cambridge site to evaluate the response of this species to the Windsor material and Milorganite during 1987.

Sewage sludge composts produced by the Beltsville Aerated pile method has been used successfully in the growing media of various non-edible horticultural crops: bedding plants (Chaney, *et al.*, 1980), container-grown woody ornamentals (Sanderson, 1980) and nursery sod production (Murray, 1981). Eggens (1982) found that composted sewage sludge was as effective as sphagnum moss peat as an organic amendent for turf rootzones receiving compaction stress.

Annual bluegrass (*Poa annua* L.) is a major component to turfs on athletic fields, lawn bowling greens and golf courses in Ontario. While it is generally considered to be a major grass weed, cultural and chemical weed control practices have been relatively ineffective in preventing its invasion into and dominance of high maintenance turf swards. Because of the extensiveness of annual bluegrass in these turf areas, turf managers have attempted to maintain it somewhat as a permanent turf cover. The results from Waddington, *et al.*, (1978) and Engle and Bussey (1979) suggests that annual bluegrass is less competitive with creeping bentgrass on putting greens when the nitrogen is from an inorganic source such as urea or a synthetic organic source such as Ureaformaldehyde than when the nitrogen source is an organic fertilizer such as Milorganite. While some researchers have attempted to relate phosphorus (Waddington, *et al.*, 1978) and micronutrients (Morgan, 1982) to this response, the reasons for this response is not well understood.

The objective of this research is to determine the suitability of the Windsor composted sewage sludge as a general turf ferilizer and compare the response of annual bluegrass to the Windsor composted sludge and Milorganite.

Materials and Methods

A preliminary study (Financed by the City of Windsor) on the Windsor composted sludge was conducted on a Kentucky bluegrass-red fescue turf on the University of Guelph campus during the summer of 1984. The turf received medium management (as a home lawn) with irrigation as required to prevent drought stress. Milorganite and Windsor composted sludge was applied (4 replications) at 0, 100, 200, 300 and 400 kg ha^{-1} every 2 weeks from June to October (8 applications).

The second study (started October 1985) was conducted at the Horticultural Research Station, Cambridge, Ontario, on a 5-year-old mixed Kentucky bluegrass, annual bluegrass, red fescue, creeping bentgrass turf. The turf received medium management and irrigated as required to prevent drought stress. Nitrogen from Urea, Milorganite, and Windsor composted sludge (+urea) was applied 8 times from April to October to supply 0, 100, 200, 400 and 800 kg N ha^{-1} over the growing season. The Windsor compost and Milorganite were applied at equal rates of product.

The third study (started July 1986) was conducted on a high maintenance putting green nursery turf mowed at 9 mm, 3 times per week and irrigated regularly. The sward consisted of approximately 70% Penncross creeping bentgrass and 30% annual bluegrass. Phosphorus and potassium were supplied according to soil test. Nitrogen was supplied as Urea or Windsor sludge compost at 0, 12 and 25 kg N ha^{-1} every two weeks.

For the 3 studies the turf response to treatment was evaluated visually using a scale of 0 to 10, 0 equalling zero or dead turf and 10 equalling ideal turf. The plots were evaluated for color, density, disease and injury from stress.

Results and Discussion

When the Windsor sludge compost or Milorganite was applied to a mixed turf on the University of Guelph campus the milorganite plots generally scored higher for green color than the Windsor compost. Milorganite had 6% N while the Windsor compost was approximately 1% N. However, after about 6 applications of equal amount of product, fertilizer burn patches appeared on the Milorganite treated turf (Table 1). Similar injury did not appear on the Windsor treated turf.

Table 1. The effect of nitrogen source and product application rate on a mixed turf on the University of Guelph Campus (September 1984)

N Source	Injury (% of plot)				
	Control	1 kg	2 kg	3 kg	4 kg
Windsor	0 a[z]	0 a	0 a	0 a	0 a
Milorganite	0 a	30 b	33 b	20 b	23 b

[z] a-b means followed by the same letter are not significantly different = 0.05 (DMRT).

In the second study at the Horticultural Research Station the turf on plots treated with Urea, Milorganite and Windsor compost (+urea) were similar at all N rates (Table 2). The color of the turf became darker green as the nitrogen rates increased. The time period involved was too short to result in any observable change in the botanical composition of the sward, thatch accumulation, stress susceptibility or proneness to disease. This study will continue for several years.

Table 2. The effect[y] of nitrogen source on a mixed turf at the Cambridge Research Station.

	N	1985	1986					
N source	rate (kg ha^{-1})	Oct 23	Apr 18	May 19	June 20	July 22	Aug 6	Sept 15
Control	0	7.0[z]	6.8a	6.9a	6.3ab	6.2a	6.5ab	6.5ab
Windsor	100	6.5a	6.5a	6.5a	6.0a	6.8b	6.5ab	6.5ab
Windsor	200	7.0a	7.3a	6.3a	6.5ab	6.8b	6.8ab	6.5a
Windsor	400	6.8a	7.0a	6.8a	7.0b	7.8c	7.3b	7.8c
Windsor	800	7.5a	7.3a	7.3a	8.0c	7.8c	7.8c	8.8c
Milorganite	100	7.0a	6.8a	6.3a	6.3ab	6.8a	6.5ab	6.5a
Milorganite	200	7.0a	6.5a	6.5a	6.3ab	7.0b	6.8ab	7.0b
Milorganite	400	6.5a	6.3a	6.8a	6.8ab	7.0b	7.0b	7.3b
Milorganite	800	7.5a	7.3a	6.8a	7.8c	7.8c	7.8c	8.0c
Urea	100	7.3a	5.8a	7.0a	6.8ab	6.8a	6.5ab	6.8ab
Urea	200	6.5a	6.3a	6.8a	6.5ab	6.5a	6.8ab	6.3a
Urea	400	7.0a	6.0a	7.0a	6.8ab	7.0b	7.3b	8.0c
Urea	800	7.3a	7.0a	7.0a	6.8ab	7.0b	7.8c	7.8c

[z] a–c means followed by the same letter are not significantly different P = 0.05 (DMRT).

[y] Visual observation on a scale of 0 to 10, with 0 equalling dead turf and 10 equalling dense, dark green turf.

Table 3. The effect[y] or nitrogen source on a Penncross annual bluegrass putting green nursery turf (July to Sept).

N source	N rate (kg ha^{-1})	July 24	Aug 8	Sept 5
Control	0	6.3a[z]	7.0a	7.0a
Windsor	12	8.7b	9.3b	7.7b
Windsor	25	9.3b	9.3b	8.0b
Urea	12	9.0b	8.3b	8.0b
Urea	25	10.0b	9.7b	7.7a

[z] a-b means followed by the same letter are not significantly different P = 0.05 (DMRT).

[y] Visual evaluation using a rating system of 0-10 with 0 representing dead turf and 10 ideal turf.

In the third study on a Penncross creeping bentgrass nursery, the turf on plots receiving the Windsor compost and urea were similar. No injury was observed on the Windsor compost plots. Some "speckling" injury, common on turf treated with urea, began to appear on 5 Sept 86. The time period involved was too short to result in any other observable differences.

Conclusion

The studies reported here were of very short duration, too short in fact, to make any specific conclusions. One observation is valid however. When applied at high rates Milorganite had a very objectionable odor while no observable odor was noted from the same high rates of the Windsor sludge compost.

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WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY -- PHASE I, INVENTORY AND DATA COLLECTION

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Introduction

The pharmaceutical manufacturing industry is a complex one. A great many chemical substances are used in relatively small quantities. The grouping of products in this industry is much more a function of the uses of the formulations to treat specific types of diseases than of their chemical nature or kind of hazards they may represent. The formulator must be concerned with meeting strict standards on toxicity, long-term stability, taste, odour, solubility and appearance. One would expect a high fraction of wastage in consequence. In fact, the reverse is true; such close control is exercised on the purity of raw materials and at each stage in the processing and packaging that wastage is minimal, and, as will be shown, the quantities of wastes produced are small.

The first phase of this study has been concerned with data collection for an inventory of types and quantities of wastes produced, and their present modes of disposal, as reported by the manufacturers themselves and by certain major users. The objectives to be achieved in this phase were:

(a) To estimate the types and quantities of wastes;
(b) To determine present disposal practices (and incidentally to estimate the costs of disposal;
(c) To identify hazardous waste streams or classes of liquid or solid wastes which might qualify under Regulation 309 as hazardous.

Methodology

A questionnaire had been prepared by the Ministry of the Environment, which we obtained in late 1985 and used as the basis of a considerably modified one. This we sent in January of this year to about 70 manufacturers and institutions. We have received replies from 35 establishments, including 6 hospitals. The others we have tried to elicit replies from by follow-up letters and repeated telephone calls, without success. Our original list was longer, but a number of firms have either closed or ceased manufacturing operations. Table 1 lists the responding manufacturers, and their chief products. We understand that the Ministry will approach non-respondents shortly, to encourage their participation.

The list of recipients of the questionnaire included nearly all the leading pharmaceutical manufacturers in the Province of Ontario, plus three large hospitals in Toronto, two smaller ones in Peterborough, and one each in Campbellford, Lindsay and Port Hope, and a few distributors and repackagers. We are pleased with the response; a 50% return from a mailed questionnaire is a fair return. We are grateful to the managers and employees of those establishments that took the trouble to reply to our questionnaire, and especially to the three firms, Connaught Laboratories in Toronto, Pfizer in London and Johnson & Johnson in Guelph, and to Toronto General Hospital, who invited us to visit them to clarify the purpose and significance of our questionnaire, and to enable us to explain to them our objectives, and to explain also the relevance of Regulation 309 to our study and to their operations.

The questionnaire is reproduced below as Appendix A. It divided the products of the industry into eleven categories, by end use. For each category the respondent was asked for answers to four questions: typical quantity disposed of annually, whether any are "Liquid Industrial Wastes", method of disposal and annual disposal costs. Twenty-two other questions are asked most of which require only "Yes" or "No" answers. They cover information about the company and its products, and certain aspects of company policy and practice with respect to waste management.

Results

A summary of the responses received forms Table 2, in the same format that was used in the questionnaire. As may be seen from the Table, the total quantity reported of all wastes is not large, being only a little under 250. tonnes, or assuming that the non-respondents will eventually produce similar figures, 500 tonnes in all. This is a minute fraction of the annual chemical waste disposal total for Ontario.

It is not clear from the Table, but our preliminary findings suggest that, in general, good disposal practices are being followed. Much material is incinerated, and we have no reason to believe that the residues that go to landfill pose any hazard. The only doubtful practice we have come across is that certain materials are going into municipal sewers that may cause concern unless they can be shown to be biodegradable or in some way detoxified, or both. This is being looked into.

It became apparent as the results of the questionnaire were analysed that additional information was required on two points. The questions on quantity of material disposed of elicited answers that were inconsistent, in that some respondents reported the net quantities of active ingredients, while others reported gross quantities. Telephone inquiry has cleared up this difficulty in large part. The quantities reported here are gross. The second matter relates to substances other than actual pharmaceuticals, i.e., solvents, raw materials and intermediates, which were not mentioned at all. We think they should have been, and we will seek this information in follow-up inquiries.

We suspect that solvents, in particular, may prove to be an important item. Local inquiry at three hospitals has shown that quantities of solvents worth recovery and recycling are being removed by licensed carriers. One company volunteered the information that their quality control and research laboratories generated quantities of waste solvents that cost them $5,000 for disposal. There must be many companies with similar experience. If an economic system of collection and recycling can be devised, we believe that large savings may be possible. The assistance of Government or of the Ontario Waste Management Corporation may prove to be valuable.

There were very few wastes reported that are subject to Regulation 309, though a number of companies commented that small amounts of such wastes were generated, below the exemption limits. The chief exception was one report of 190,000 L of liquid industrial waste, under our category of mineral-based pharmaceuticals. At the time of writing, the Ministry's records are being searched for items reported under the Regulation.

The costs reported do not appear to be enormous. We arrived at a total of $93,700 for the 36 companies for a year, and again assuming non-responders have similar experiences, estimate a total cost for the Ontario industry of about

$180,000. This is probably not a significant fraction of the cost of doing business. Nevertheless, in certain cases economies are probably possible.

Response to Survey Questions

The twenty-three numbered questions in the questionnaire include some that are of an administrative nature, but the answers to questions that are significant in this study are summarized in Table 3. In this table, (and in Table 2) it will be noted that columns do not always add up to the noted totals, or correspond to the total number of firms replying. In most cases this is due to overlapping categories of reply, but some of the replies were somewhat confusing, and uncertain replies may have been counted in two ways. These points will be clarified where possible.

Significant aspects of the replies will be noted. Several firms mention solvent waste streams, few of which are being recycled or recovered. Only half the replying firms actually manufacture in Ontario; the rest are formulators, repackagers or distributors only. Of the actual manufacturers, 70% are in the Totonto area. The business of waste disposal is rather concentrated; one firm handles 30% of the hauling and 44% of the receiving (excluding landfill).

Corporate responsibility, or at least awareness, in this field seems good. Most of the firms report the use of waybills (presumably all that dispose of significant amounts of hazardous substances); most have explicit policies and guidelines on disposal of toxic substances. Waste reduction, treatment and recovery are subject to economic dictates. The small number of firms reporting treatment or recovery on site probably reflects the high capital cost of facilities for these purposes. Several firms report off-site recovery of solvents, in particular. (This question was not asked.) Half the firms report waste-reduction incentive schemes or other encouragement. The majority of the others are not significant generators of wastes.

Conclusions

The present report is preliminary, and is to be amplified and compared with experience in other jurisdictions, and (as noted above) with other information from Ministry files. It may already be noted, however, that the problems associated with waste disposal in the pharmaceutical industry are not severe, either in environmental or in economic terms. The only recommendation we are in a position to make is that already mentioned, that more effort should be made to encourage recovery and suitable recycling of solvents. It may not always be possible to restore solvents to the degree of purity required by the original user, but other users may have less stringent requirements. Where quantities justify the capital expense, the most convenient way is in-house recycling, but externally contracted recycling is immediately available from at least one firm.

Acknowledgements

The continued assistance of the Waste Management Branch, and a generous grant from the Ministry of the Environment of Ontario are gratefully acknowledged.

TABLE 1

Major producers of pharmaceuticals in Ontario

	analgesics	antihistamines	antitussives & expectorants	sedatives and anticonvulsants	psychotherapeutics	cardiovascular agents	corticosteroids	estrogens	antibiotics
Allen & Hanburys	x			x		x	x	x	x
Ames/Dome/Miles	x						x		x
Anca Laboratories	x			x		x			
Astra Chemicals						x			
Denver Laboratories					x				
Dow Pharmaceuticals	x	x	x		x				x
Drug Trading	x			x	x	x	x		x
Fisions (Canada)	x		x						x
Fulford Dodds	x								
Glaxo Laboratories							x		x
Lilly, Eli & Co.	x	x		x	x		x		x
McNeil Laboratories	x			x	x				
Mead Johnson	x					x		x	
Merrell, William S.								x	x
Norwich Pharmacal Co.	x								
Novopharm Ltd.	x	x		x	x	x	x		x
Organon Canada							x		
Ortho Pharmaceutical								x	x
Parke Davis & Co.	x	x	x	x		x	x	x	x
Paul Maney Laboratories				x	x				x
Pennwalt of Canada			x						
Pfizer Co.					x		x		x
Purdue Frederick Co.	x					x			
Riker Pharmaceutical Co.	x		x						x
Rorer, William H.	x				x				
Searle Pharmaceuticals				x				x	
Sterling/Winthrop	x		x	x		x			x
Upjohn Co. of Canada	x		x				x	x	x
Wampole Ltd.	x								
Warner-Chilcott	x			x		x	x		x
Whitehall Laboratories	x								
Wyeth Ltd.			x	x		x		x	x

TABLE 2

Class of Pharmaceuticals	No. of Respondents	Quantity Disposed of Annually Kilograms or Litres	Hazardous or "liquid industrial" waste (Regulation 309)	Present Method of Disposal Incineration (I) Landfill (L) Mun. Sewer (S)	Estimated Cost for Disposal Annually $(000)
Antihistamines	7	250	---	L or I	1.3
Antitussives, sedatives, anticonvulsants, anaesthetics and analgesics	8	3,100	1 (Thiamylal-Sodium) controlled drug	L/I	2.5
Psychotherapeutics	5	1,400	---	L/I	4.0
Cardiovascular agents	7	2,000	---	L/I/S	1.5
Corticosteroids	7	410	2	L/I/S	1.7
Hormones & synthetic substitutes, including estrogens	8	12	---	L/I/S	---
Anti-infective agents, including antibiotics	9	254	---	L/I/S	2.61
Biologicals, including vaccines	6	18,300	---	I/S	40.1
Antineoplastics	3	70	---	I/L	0.3
Organic-based pharmaceuticals, not otherwise specified	9	26,400	---	I/L/S	7.2
Mineral-based pharmaceuticals, not otherwise specified	2	190,000	Industrial liquid waste	I/L/S	12.1
Category not specified	3	25	---	I/S	20.4
TOTALS	36	242,221	---	---	93.7

TABLE 3

Summary of Replies to Numbered Questions

Question No.	Topic		No. Reported
6	Major hazardous waste streams		
	Solvents: halogenated		3
	non-halogenated		3
	miscellaneous		3
	Chemicals: miscellaneous		2
	rejected pharmaceuticals		2
	Pathological		1
7	Number of plants		17
8	Location of plants		
	Toronto area		12
	Belleville		2
	Aliston		1
	Lindsay		1
	Perth		1
9	Haulers		
	Firm A*	used by -	7
	B		4
	C		3
	D		2
	Seven others	(one each)	7
10	Receivers		
	Municipal or other MOE approved landfill		9
	Firm A		10
	Firm C		4
	Firm E		2
	Seven others	(one each)	7
11	Waybills used?		
	Yes		20
	No		6
12	Corporate waste disposal policy?		
	Yes		22
	No		1
13	Guidelines on disposal of toxics?		
	External		14
	Internal		10
	None (or no reply)		7
17	Waste reduction procedures used?		
	Yes		10
	No		12
	N/A		17

Table 3, page 2.

Question No.	Topic	No. Reported
18	On-site waste treatment?	
	Yes	2
	No	22
	N/A	14
19	On-site recovery or recycling?	
	Yes	3
	No	17
20	Waste-reduction incentives?	
	Yes	16
	No	7
	N/A	16

*Firm names on file with Ministry of the Environment, as Appendix B to this Report.

"Development of Guidelines for the Utilization of Industrial Waste in Backfill and Construction Applications",

G. Zukovs,
Canviro Consultants Ltd.
Toronto, Ontario

This paper will be distributed at the Conference.

Numerical and Laboratory Modelling of Two-Phase Flow in Porous Media: I. Two-Phase Gaseous Flow. II. Two-Phase Liquid Flow

by

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Abstract

Numerical and laboratory modelling of two-phase fluid flow in porous media is taking place under a larger project "Assessing the Impact of Hazardous Liquids Spilled Onto Soil". Numerical models to simulate two-phase liquid and vapour situations have been developed, and early verification against laboratory data has produced very good results. Liquid phase experiments are monitoring the migration of an immiscible liquid through a 60 cm. water-saturated vertical sand column. Relative liquid saturation behind the intruding front is monitored to steady-state with the thermal conductivity probe developed at the University of Waterloo. Relative permeability curves as a function of oil and water relative saturations have been developed.

Two phase gaseous flows are being modelled in a flux chamber. Hexane as a liquid is introduced in a pan and allowed to volatilize and migrate away from the source. Numerical and laboratory results are compared to determine soil absorption properties and variabilities in the parameters governing hazardous diffusion in porous media.

Research on the behavior of hazardous immiscible liquids (HIL's) in soil supported by the Ontario Ministry of the Environment has been in progress since January, 1984. This paper provides a general review of the project accomplishments to date as well as some results from recent experiments on the movement of HIL's and their vapours in soil.

GENERAL REVIEW

1.0 Modelling

1.1 Spill Propagation Models

Spill propagation models were developed to aid in understanding how spills of HIL's form, move outward and penetrate the soil. They were also designed to assist with spill remediation by providing a rapid simulation of the lateral and vertical spreading of the liquid. In this regard, the work has made an important contribution to the science of HIL spill management, providing the first models of their kind for HIL's.

Wall Model

The Wall Model (Wall, 1984) for spill propagation is based on the St. Venant equations for liquid flow in 2-D axis-symmetrical coordinates. It includes components which simulate evaporation and infiltration from a growing pool of spilled HIL and is able to conserve both mass and momentum. The equations are solved by approximate numerical methods in a computer code. Spill experiments were performed in part to permit model verification. Model simulations of the experimental data were reasonably good although the model did not handle as well as expected, the differences in contact angles between HIL's and the spill surface. The model, while quite accurate in its simulations, is rather expensive to use. Consequently, a second model was developed.

MBPF Model

The MBPF Model for spill propagation is an empirical model based on the work of Raisbeck and Mohtadi (1974). It was adjusted to accommodate; spill surfaces at various angles, variations in the contact angle between the HIL and the surface, evaporation, and infiltration. Both laboratory and field experiments provided a basis for testing the model. The model was able to simulate the experimental data quite well.

1.2 Liquid Penetration Model

The Osborne-Sykes Model (Osborne, 1984) for penetration of HIL's through soil was developed and tested during this research programme. The model solves the partial differential equations describing intergranular porous media flow equations (Bear, 1970) adjusted to handle immiscible liquids. The equations are solved in 2-D by means of a finite element method computer code.

The model was subsequently used to simulate the results of laboratory scale experiments on the movement of HIL's in soil columns. The experiments are described below. The simulations performed did not fit the data particularly well (predicted velocities were twice that of measured values). This was attributed in part to the hydraulic conductivity and capillary pressure versus saturation data used as input for the model. Actual data for the HIL's used were not available and thus substitutes were used. Experiments are now in progress in order to provide such data for the specific liquids used. Since the simulations generated were of the correct form and magnitude, it is felt that the model performs well.

The availability of the Osborne-Sykes Model is a significant contribution to solution of HIL spill problems. It can provide useful estimates of how a spilled liquid will behave in the soil; how deeply it will penetrate, how it will behave at the zone of saturation and what will occur if the liquid peentrates the zone. Such information would be most helpful in the design of remedial measures at the site and in assessing the severity of the problem.

1.3 Vapour Transport Model

The Allan Model (Allan, 1986) was developed to simulate the movement of vapours from HIL's in soil, a problem of growing concern at spill sites. The model is a 2-D finite element solution to a system of intergranular porous media flow partial differential equations. It is based on a landfill gas migration model developed previously under NSERC sponsorship. It has been tested against field data and the results from a limited number of laboratory scale experiments to be described subsequently. The comparisons between the two have been excellent.

The value provided by the Allan Model lies in its capacity to simulate the extent of suspected problems and to evaluate the success of vent or barrier control methods. It may also be of use in helping to track the movement of the actual liquids themselves.

2. Experimentation

Experimentation was performed with several objectives in mind; to provide information about the movement and retention of HIL's onto and into soil under both laboratory and field conditions, to produce a data base for use in calibrating the models developed in the work, and to develop experimental methods and equipment suitable for the study of HIL and vapour movement in soil.

2.1 Spills

Laboratory: Small Scale

Ethylene glycol and hexane as examples of HIL's were spilled from various heights through a 2.0 cm orifice onto an impervious surface either flat or inclined and either smooth or rough. Liquid volumes up to 5 litres were used. Video cameras were used to collect time dependent data on spill diameter, depth, hydraulic jump location and flow rate (source liquid height). The spill propagation models, as mentioned above, were then used to simulate the spill for the specific conditions of liquid viscosity, mass density, contact angle, discharge height and flow, and surface roughness and inclination.

Field Scale

Large scale spills were carried out in co-operation with the firm of S.L. Ross in Ottawa using both impermeable and sodded soil surfaces, either flat or inclined at 10°. Up to 200 L of liquids with viscosities ranging from 1 to 65 cp were spilled onto the various surfaces at rates ranging from 22 to 95 $\ell\ .\mathrm{min}^{-1}$. A total of 27 experiments were completed. The data recorded with respect to time included bore and hydraulic jump locations, depths, runoff and infiltration.

The spills were simulated using the MBPF model with good fits produced. The model roughness coefficient (n) was used as a fitting parameter with values ranging from 0.005 for a painted surface to 1.75 for a sodded surface.

Both sets of spill experiments provided useful quantitative data about the spreading and infiltration of HIL spills in response to variations in fluid type, spill rate and receptor surface slope, roughness and permeability. Similar data from other sources were extremely limited prior to this work. The experiments also provided a data base from which spill models could be developed and tested.

2.2 Liquid - Soil Interactions

Penetration Experiments

Experiments were, and are being performed in laboratory scale columns (7.3 cm diam. x 61.1 cm long) with HIL's being allowed to pass through sandy soil under continuous flow conditions. Liquids including oils, hexane, decane and perchlorethylene, are loaded to the columns at various flow rates and antecendent soil water contents. Measurements are made to determine the rate of movement of the HIL into the soil. Important information on transport velocities as influenced by liquid viscosity, density and contact angle and soil moisture and permeability has been obtained. Very little similar information was available prior to this work. It has provided insight into the nature of HIL movement through soil as a result of a spill. It has also provided a useful data base from which model evaluation can be made. This was, in fact, done for for the Osborne/Sykes Model. As noted previously, however, the model simulations were only fair because of limitations in the input hydraulic conductivity and capillary pressure data. Some recent results are presented subsequently.

Storage and Leaching of HIL's in the Unsaturated Zone

Experiments are being carried out in soil columns to determine the short- and long-term ground water contamination potential from a spilled HIL held in the vadose zone. Soil columns at various antecendent moisture levels are subjected to large volume oil spills. The oil is allowed to diffuse through the soil profile for a period of days. Effluent is collected, and the relative volumes of oil and water are determined with a centrifuge. Once the profile has stabilized (i.e. no further drainage of oil or water), pulse "rainfall" treatments are introduced at three day intervals. These data are being utilized to develop time and mass dependent contaminant removal curves.

The experiments, though begun only recently, have already provided significant insight regarding the residual HIL storage in the vadose zone as related to antecedent soil mositure conditions at the spill site. One anticipated recommendation will address immediate data collection of site soil mositure conditions by the spill response team. These data will allow accurate predictions of the HIL quantity remaining in the vadose zone, and estimation of the rate of contaminant leaching by infiltrating precipitation.

Several other liquids, including hexane, heptane, perchlorethylene and cyclohexane, are under consideration for use in this experiment.

Detection Methods

Detecting the movement of a HIL as it displaces the native soil fluid at a point, proved to be a challenge in this research. Methods based on polarity and dielective constant differences between the fluids were tried but proved difficult to use. Finally, a thermal conductivity probe was devised consisting of a heating coil surrounding a thermocouple with a total diameter of 3 mm and a length of 12 cm. A predetermined amount of current is passed through the probe for a fixed time and the rise in temperature as a function of fluid thermal conductivity is measured. The reproducability of the probe response is excellent. Subsequent experiments to detect the passage of a HIL through water-wetted soil have given very good results. The development of this probe has enabled non-destructive experiments to be conducted on continuous HIL flow in porous media. This is a major achievement. Work to develop the probe into a unit for the detection of HIL movement in the field is planned.

2.3 Vapour in Soil

Experiments have been conducted on the movement of gases and vapours in soil. The initial work was performed using gases such as methane for ease and comparative safety during the equipment and methods development stage.

Gas was introduced at the top or bottom of vertical, cylindrical soil columns, 8 cm dia. and 42 cm long. Samples were extracted in syringes and analyzed in a gas chromatograph with respect to time. The data exhibited diffusional behavior as anticipated and were used to test the Allan Model for gas migration.

Subsequent experiments are in progress using hexane and acetone in the column foot space as a liquid source to emit vapours for migration through the column. Data on vapour concentrations and emission rates have been collected. Limited model simulations have been done.

Construction of a large vapour flux chamber plus fume hood has been completed and will be used for large scale experiments on vapour movement in soil. Preliminary experiments have been completed.

EXPERIMENTS ON IMMISCIBLE LIQUID TRANSPORT IN SOIL

Immiscible fluids are of environmental concern today because:

- the variety and quantity of immiscible liquids have steadily increased,
- many of the immiscible liquids are toxic and/or carcinogenic,
- although only slightly soluble, immiscible liquids are often soluble at concentrations which are above levels considered safe, and
- immiscible liquids in soil being poorly soluble remain as a source of contamination for many years.

It is important to understand how immiscible liquids migrate through the ground because of the potential danger they pose to groundwater.

The theory of immiscible displacement was developed and put into practical use in the petroleum industry some time ago to assess the behavior of oil and gas in reservoirs and to optimize the effects of steam and water-flooding. However, the application of immiscible displacement theory to groundwater contamination scenarios is a relatively new practice. It is only in recent years that research in this area has taken place. The three major areas of research over this time are worthy of note.

One area of research has involved the movement of hydrocarbons from the surface of the ground to the top of the water table. Hydrocarbons are lighter than water and therefore do not migrate past the water table. Analytical expressions were developed to describe the movement of hydrocarbons in simplified situations and to find the distribution of water, air, and the hydrocarbon in the ground. Laboratory experiments were performed in sandboxes and columns to watch the movement of the hydrocarbon front and to get estimates of residual saturations. Papers in this area include work by Van Dam (1967), Schwille (1967), Mull (1971), Schiegg (1977), Dracos (1978), and Eckberg and Sunada (1984).

Another area of research has examined the migration of hazardous compounds that are heavier than water, most notably the low molecular weight solvents. These immiscible liquids being heavier than water generally sink past the groundwater table. They continue to move down until all the fluid is at residual saturation, or until an impermeable layer is reached, or until a layer with an entry pressure greater than the pressure that can be built up by the infiltrating fluid is reached. This research has looked at the migration of compounds in sandboxes and sand columns in different situations. Migration in the saturated and unsaturated zones were examined and the residual saturation of various compounds were investigated. This work was carried out mainly by Schwille ((1967), (1975), (1984)).

The newest area of research is the quantitative evaluation of contamination of groundwater by immiscible liquids. This involves the development of complex finite element or finite difference computer models to predict the movement of immiscible liquids in the ground. The most recent models in the literature include those of A.D. Little (1983), Faust (1985), Abriola and Pinder (1985), and Osborne and Sykes (1986). Verification of these models is done by comparing their results to the results of another model or to the 1-D analytical solution of Buckley and Leverett (1942).

The purpose of this research has been to further this understanding of the migration of immiscible fluids in soil and to furnish experimental data which can be used to verify simulation models.

1. Detection Methods

No standard method exists to measure the saturation of two immiscible liquids in a porous media as a function of time and location. However, a device is being developed as part of this work to make such measurements. The device, a thermal conductivity (TC) probe, consists of a "thermo" part or coil which pulses a certain amount of heat for a specified period of time and a "probe" part or senser which measures temperature. Depending on the thermal conductivity of the material(s) between the coil and the senser, a certain change in the temperature is experienced at the senser each time a pulse occurs. Since most immiscible liquids of a hazardous nature have a thermal conductivity approximately one-quarter that of water, it was felt that this device could be made to detect changes in the amount of water and immiscible liquid surrounding the probe.

The first step in development of the TC probe was to optimize the configuration of the probe so as to obtain the maximum measured temperature change between water and an immiscible liquid for a given pulse of heat. Several designs were tested and compared by taking temperature measurements in oil and water and looking at the difference in the measurements (ΔT) for each probe.

Based on maximum ΔT, the configuration shown schematically in Figure 1 was considered the best.

The second step in developing the TC probe was to examine the relationship between ΔT and spatial mixture of the immiscible fluids surrounding the probe. It was felt that a linear relationship would exist between ΔT and the % mixture of the immiscible fluids surrounding the probe.

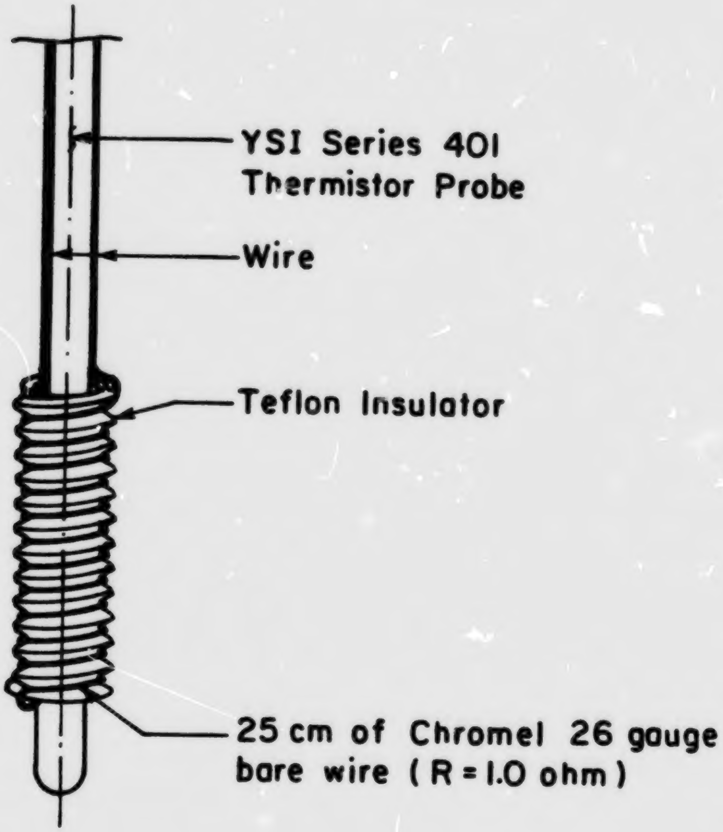
Attempts were made to make homogenous mixtures of different concentrations of oil and water. The change in temperature could then be measured by the probe for each mixture and a plot of the temperature change per heat pulse versus % oil (or water) made. Attempts to make homogeneous mixtures of oil and water were made by using conventional blenders, homogenizers, and by mixing by hand in a porous media. However, in each case the oil would start to separate from the water once mixing was stopped. Emulsifiers were then employed to keep the oil and water from separating. Both "Span-80" and "Triton" were used for this purpose with reasonable success as shown in Figure 2. While some scatter in the data are evident, there is clearly a linear relationship between ΔT and percent saturation (% H_2O in mixture). It is also shown that the presence of the emulsifier did not have a major effect on the ΔT response.

The third step in developing the TC probe was to look at factors that might change the reading of the probe other than just the spatial mixture of the immiscible fluids. The factors which were considered were the initial temperature of the fluids, the velocity of the fluids, and the previous wetting history of the soil. The effect of initial temperature of fluid on ΔT was found not to be significant. This was done by taking readings from the probe in water baths at temperatures from 18° C to 40° C. The ΔT readings showed no significant change over this temperature range.

The consequence of different fluid velocities would have on a reading was looked at by placing the probe in a column of saturated porous media. Water was passed through the column at various velocities and the probe readings recorded. The results indicate that, at higher velocities in the range of 3.0 cm.min^{-1} or greater, there is a significant effect on ΔT. However, a preliminary correction factor for this error has been established. For the range of velocities that have been expected with oil flow in soil (up to 0.4 cm.min^{-1}) the effect of velocity on ΔT can be neglected.

The experimentation done to assess the impact of previous wetting history on ΔT was done by placing the probe first in water, then in oil and then back into water. The readings recorded when the probe was in the water for the second time were initially different from the readings

THERMAL CONDUCTIVITY (TC) PROBE


YSI Series 401
Thermistor Probe
Wire
Teflon Insulator
25 cm of Chromel 26 gauge
bare wire (R = 1.0 ohm)

Scale : Two times actual size

Figure 1

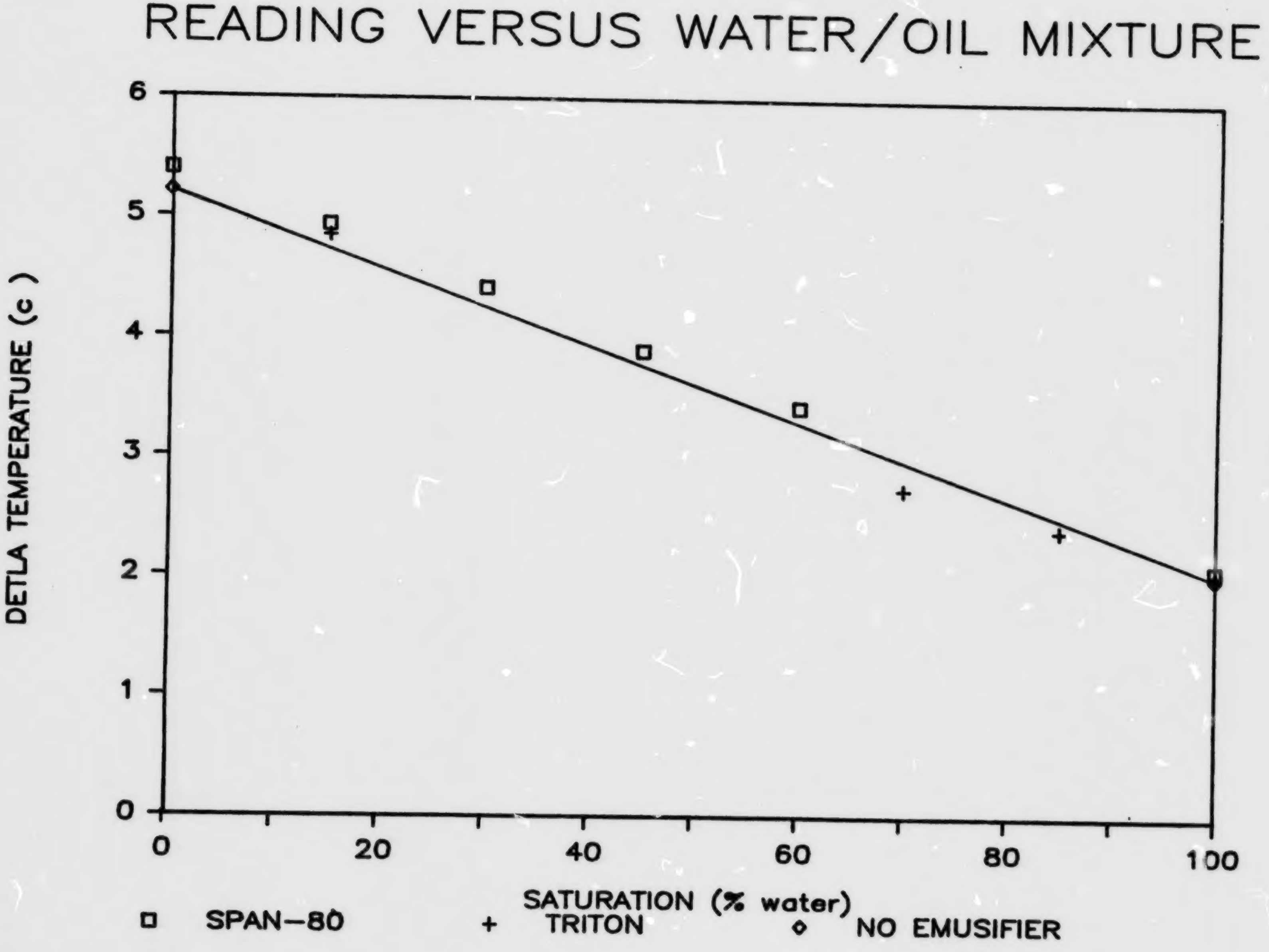

READING VERSUS WATER/OIL MIXTURE
DETLA TEMPERATURE (c)
0
1
2
3
4
5
6
0
20
40
60
80
100
SATURATION (% water)
□ SPAN–80
+ TRITON
◇ NO EMUSIFIER

Figure 2

recorded from when the probe was first in the water. However, the second readings gradually approached the first during which time, a visible film of oil appeared on top of the water. Thus, the wetting history did not appear to have a significant effect on ΔT if sufficient time were available between measurements. As well, in a porous media it is unlikely that such rapid changes in the spatial mixture of immiscible liquids as used in this experiment would occur.

2. Column Experiments On Immiscible Liquid Transport

Several experiments have been performed to examine the movement of immiscible liquids in soil to provide a basic understanding of the processes involved, to test the TC probe and to quantify the transport as a data base for model evaluation. The equipment used was described previously. The liquid used was coloured oil for the initial development work. However, other hazardous liquids are now being studied. All experiments involved upflow imbibition of oil into water saturated sand at constant heads (6 cm H_2O). Two TC probes were located in the 54 cm depth of sand at 21 cm and 40 cm up from the bottom.

The results of two experiments are shown in Figures 3, 4 and 5. Figures 2 and 4 show the experimental data recorded as ΔT, the lower and upper TC probe output versus time measured from the time of oil entry to the column. Since the thermal conductivity of the oil is less than H_2O, ΔT for oil is greater. Relative saturations range from 100 H_2O (0% oil; $\Delta T \approx 1.25°$ C) to 0% H_2O (100% oil; $\Delta T \approx 1.85°C$). The results show that the oil front was only slightly dispersed with passage from 0 to 100% oil occurring in approximately 20 minutes at the lower probe. The oil used in Experiment 3 was more viscous than for Experiment 2, producing a lower permeability and a slower velocity as shown in a comparison between Figures 3 and 4. The data appear to be very good with only limited scatter.

Figure 5 compares the results from Experiments 2 and 3 by normalizing the data from ΔT values to % oil saturation and by adjusting the time axis from Experiment 3 to that of Experiment 2 because of viscosity differences due to different experimental temperatures. This comparison at the lower probe is excellent with a 10 minute differential shown at the upper probe. The favourable comparisons between the two experiments are a measure of TC probe reliability.

The information shown in Figure 6 is in the form of fluid velocity with respect to time for Experiments 2 and 3. As the theory related to the Darcy Equation states, the velocity of the fluid mixture within the column will reduce as the % oil in the column increases. Oil travels more slowly than water and, because of the upflow configuration, the oil regulates the flow. As the height of the oil increases, the hydraulic gradient also reduces. Thus, the first order decay in velocity as shown in Figure 6 is reasonable. Normalized comparisons between Experiments 2 and 3 are excellent.

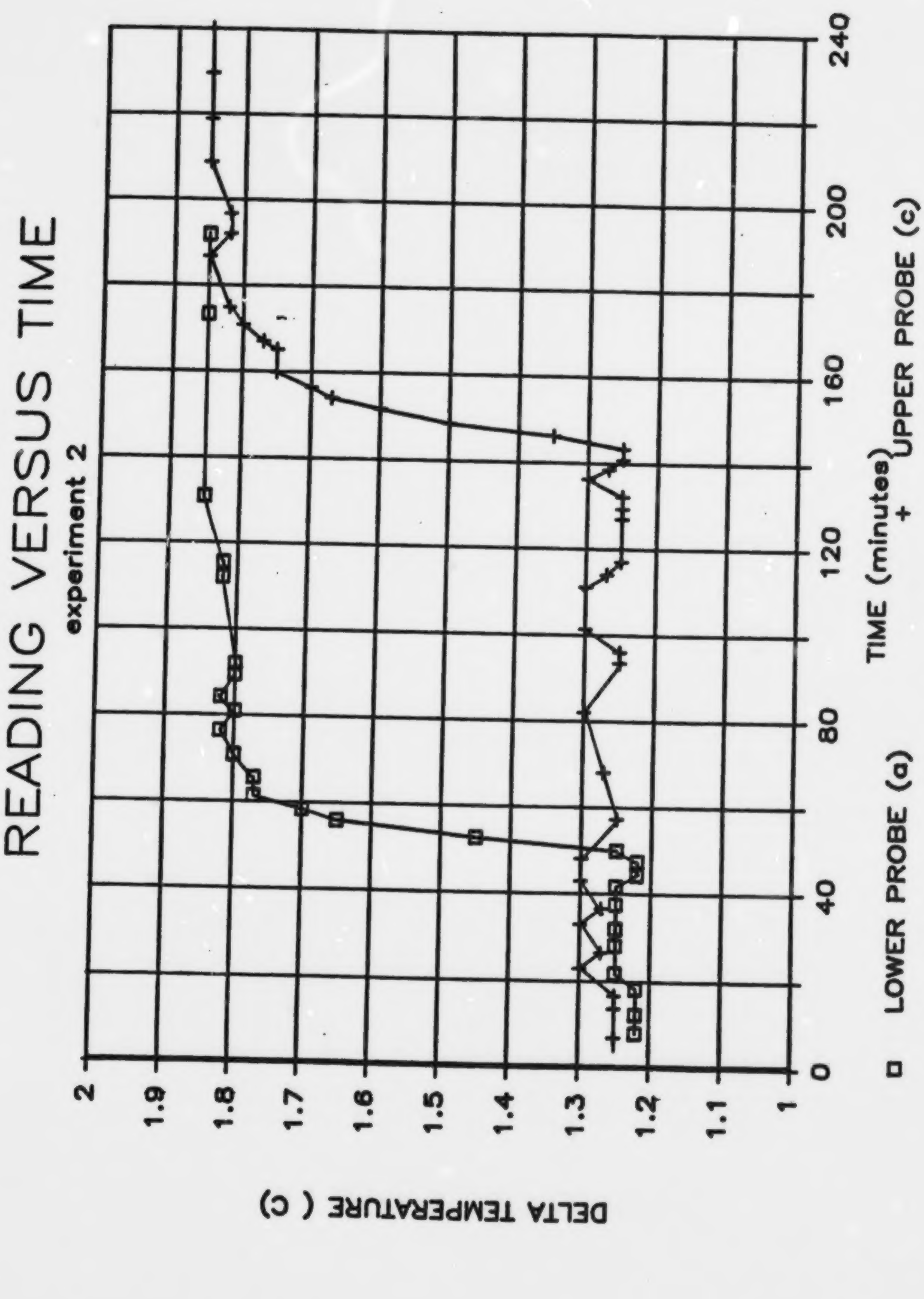

READING VERSUS TIME
experiment 2
DELTA TEMPERATURE (C)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0
40
80
120
160
200
240
TIME (minutes)
□ LOWER PROBE (a)
+ UPPER PROBE (c)

Figure 3

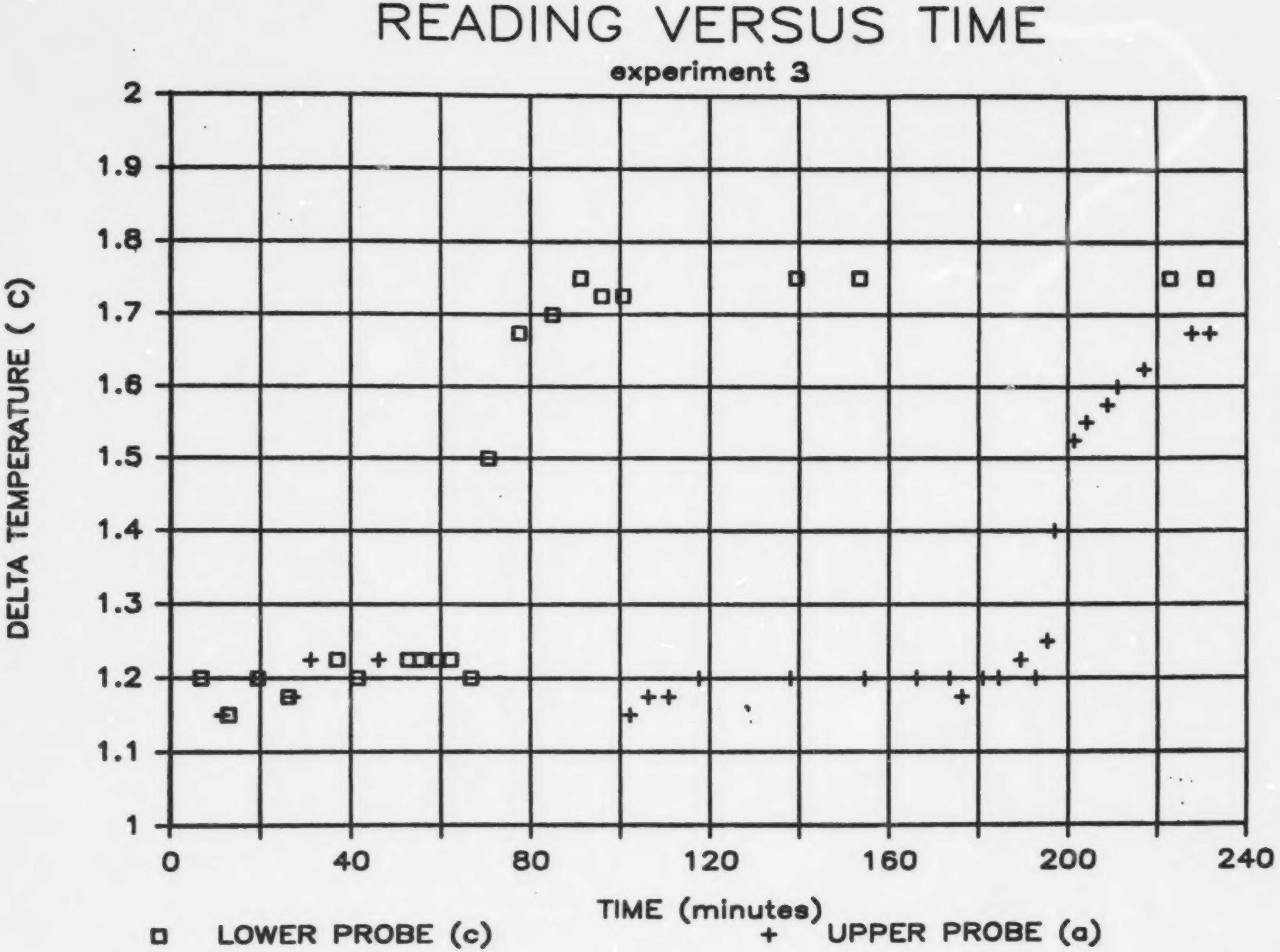

READING VERSUS TIME
experiment 3
DELTA TEMPERATURE (C)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0
40
80
120
160
200
240
TIME (minutes)
□ LOWER PROBE (c)
+ UPPER PROBE (a)

Figure 4

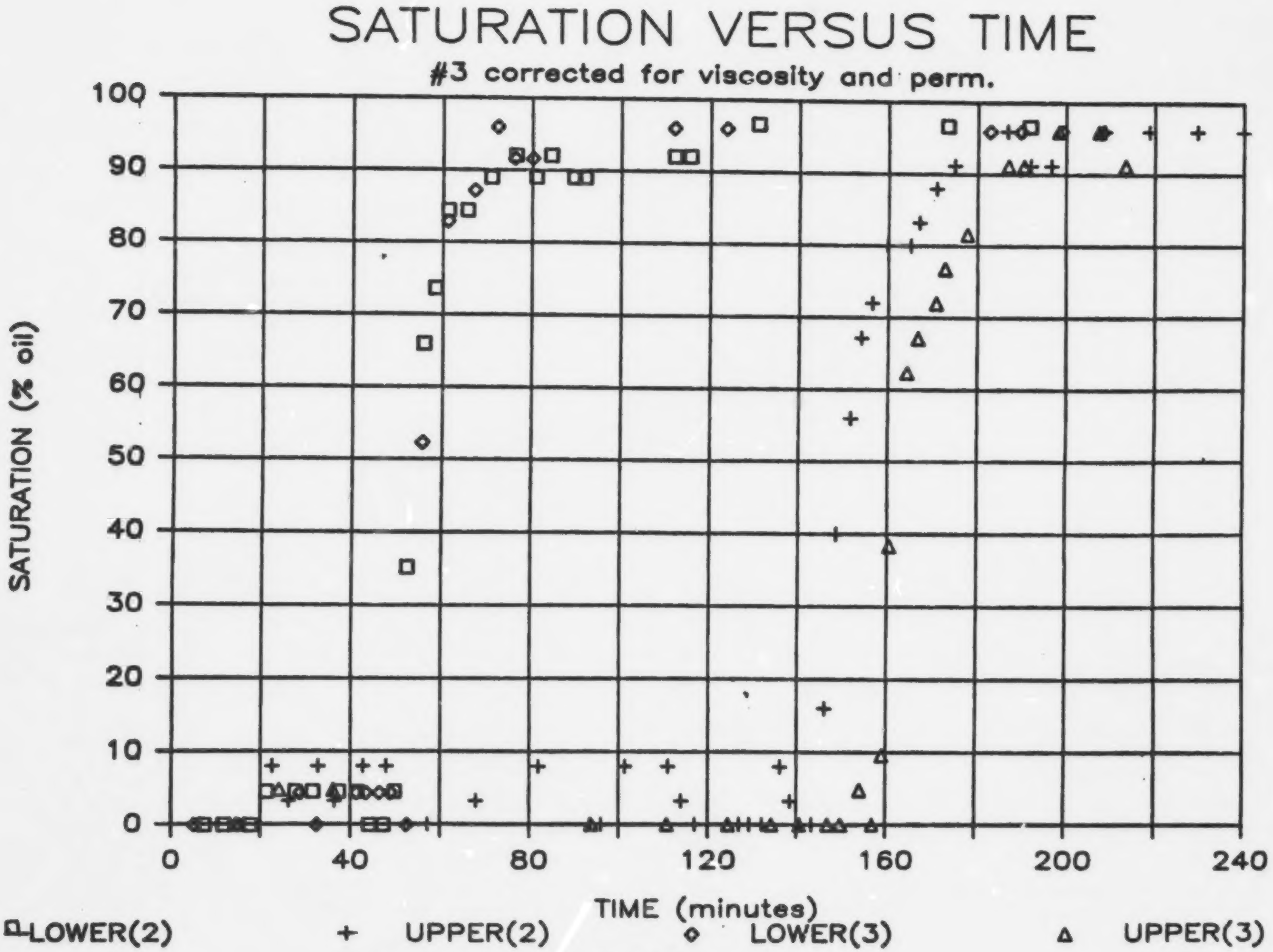

SATURATION VERSUS TIME
#3 corrected for viscosity and perm.
SATURATION (% oil)
100
90
80
70
60
50
40
30
20
10
0
0
40
80
120
160
200
240
TIME (minutes)
□ LOWER(2)
+ UPPER(2)
◇ LOWER(3)
△ UPPER(3)

Figure 5

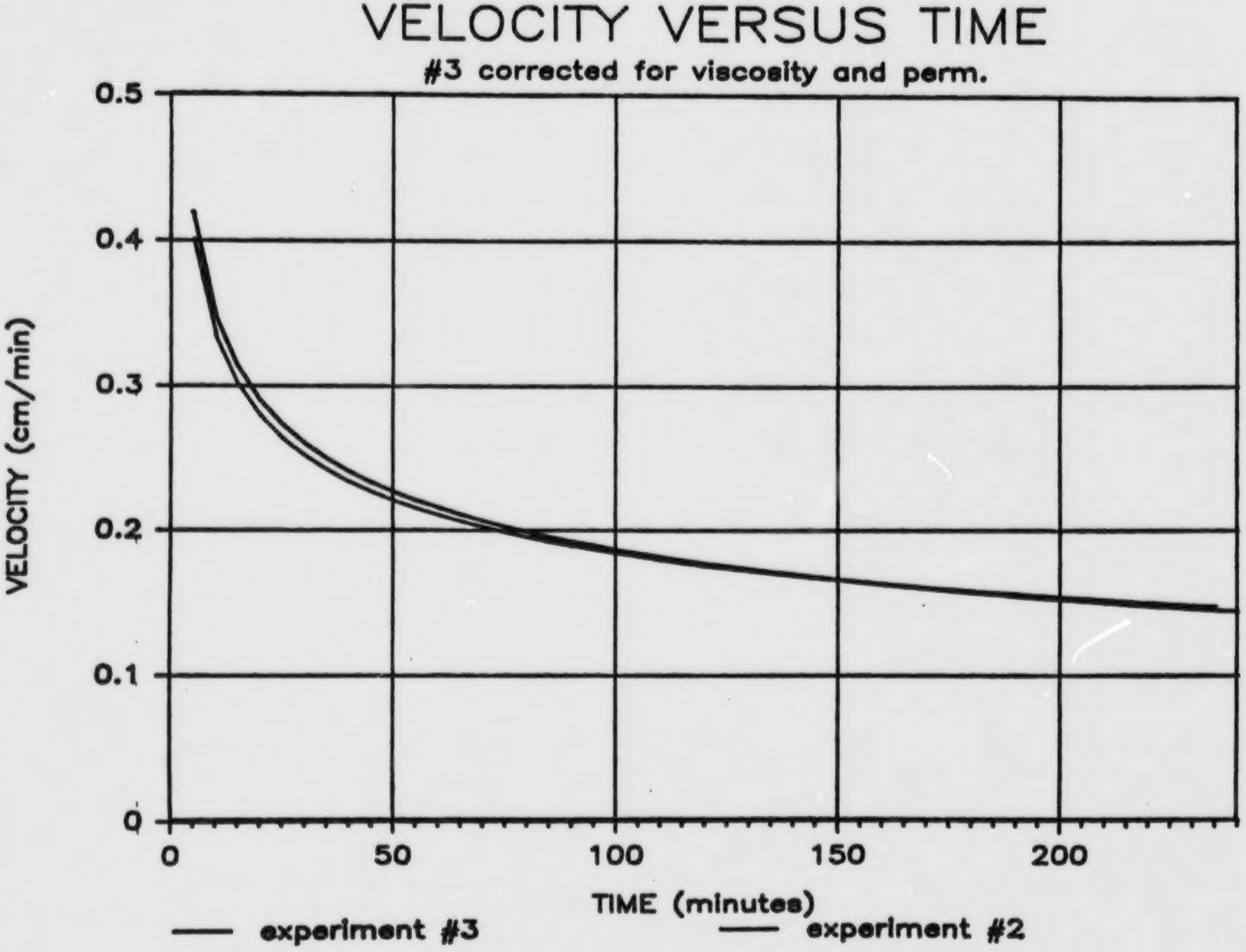

VELOCITY VERSUS TIME
#3 corrected for viscosity and perm.
VELOCITY (cm/min)
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
200
TIME (minutes)
experiment #3
experiment #2

Figure 6

3. Measurements of Relative Permeability and Capillary Pressure vs. Relative Saturation

Relationships between relative permeability and capillary pressure versus relative saturation are essential to quantifying movement of multiphase fluid systems in soil. As identified previously, limited experimentation of this nature has been done for oil-water mixtures but very little for other immiscible liquids. Consequently, this experimental series was designed to fill this need by developing improved experimental methods and then applying them to liquids other than oil.

The experimental method involved use of the standard column of this research to which varying proportions of oil and H_2O were added at constant flow rates. Steady state was defined as the point at which the oil-H_2O proportions of the effluent became steady. The combined discharge velocities and the applied pressure heads were used to calculate the relative permeabilities. The results of the first experiment performed are shown in Figure 7. This is for the drainage curve and since the relative permeability curves are hysteretic, the imbibition curve will also have to be developed.

Although the results are preliminary, they have the proper form and thus confirm the utility of the method chosen. It must be noted that these experiments are non-destructive because of the use of the TC probe. All prior experiments have required that, for each pair of points on the curve, the column be taken apart and the relative saturation be determined using a separate experiment. The continuous flow, non-destructive method developed here is thus a great improvement in methodology. It will be subsequently applied to other immiscible liquids in this work.

The results of preliminary experiments to quantify capillary pressure versus % water saturation for drainage conditions are shown in Figure 8. In this case water is the wetting fluid and oil is the non-wetting fluid.

EXPERIMENTS ON VAPOUR MOVEMENT IN SOIL

The movement of hazardous vapours in soils is being examined on two different scales. Soil columns 7 cm in diameter and 36 cm high have been utilized to study the movement of methane, hexane and acetone vapours through fine sand. A large rectangular chamber referred to as a flux box has also been constructed, together with the necessary safety exhaust system. The box has been constructed so that either gases, such as methane, or liquids, such as hexane, heptane or acetone, may be exposed to the soil. Preliminary studies with the flux box are being carried out with methane. Once experimental procedures have been refined, tests will be carried out with one or more of the volatile HIL's.

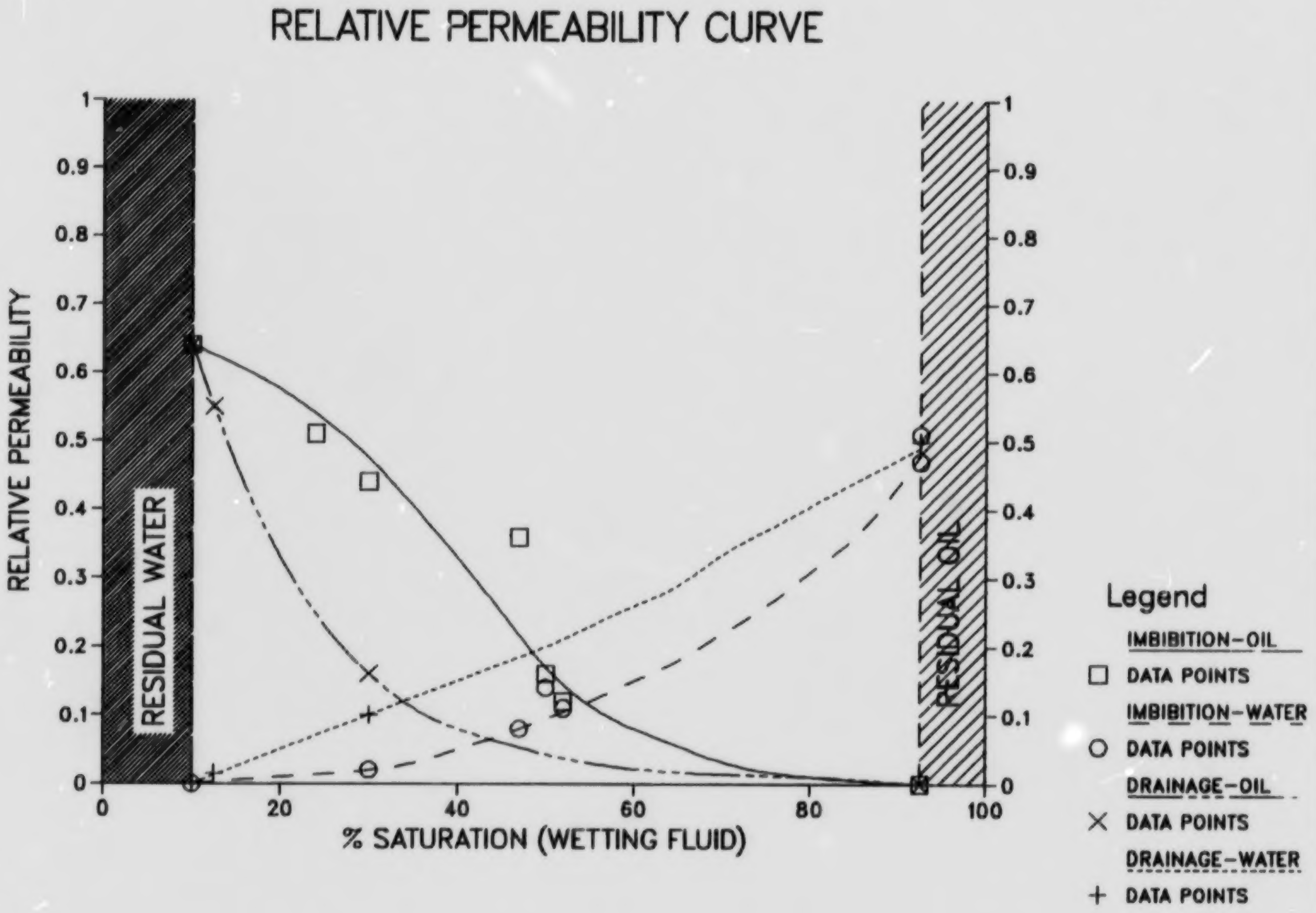

RELATIVE PERMEABILITY CURVE
RELATIVE PERMEABILITY
% SATURATION (WETTING FLUID)
RESIDUAL WATER
RESIDUAL OIL
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
20
40
60
80
100
Legend
IMBIBITION-OIL
□ DATA POINTS
IMBIBITION-WATER
○ DATA POINTS
DRAINAGE-OIL
× DATA POINTS
DRAINAGE-WATER
+ DATA POINTS

Figure 7

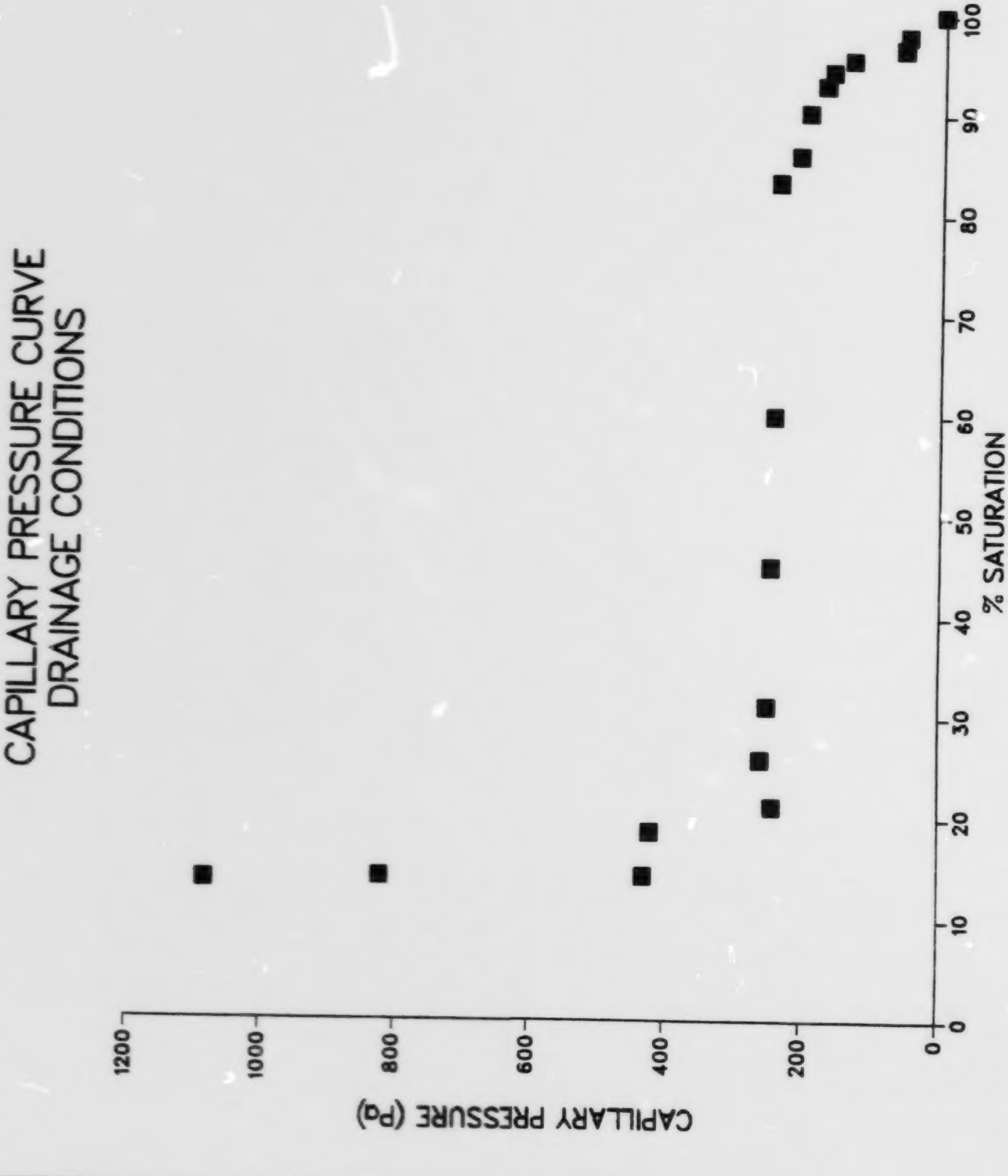

CAPILLARY PRESSURE CURVE
DRAINAGE CONDITIONS
CAPILLARY PRESSURE (Pa)
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
100
% SATURATION

Figure 8

1. Soil Column Experiments

Plexiglass cylinders containing a fine Ottawa sand serve as the test columns identified above. The ends of the column are closed except for two ports for the introduction of vapour and for pressure control. An open volume approximately 5 cm high is maintained at the top (head space) and the bottom (foot space) of the column. A gas contaminant can be introduced into either end of the column, depending upon experimental protocol. A small airflow is introduced at the opposite end to insure that no contaiminant build-up occurs thus maintaining a zero concentration condition at the discharge boundary end. The pressure ports maintain atmospheric pressure in the head and foot spaces. Therefore, the only vapour migration into and through the soil is due to diffusion and for body forces.

Sampling ports are located at 7.5, 15.0, 22.5 and 30.0 cm from the contaminant source. Sampling methods to date have utilized syringes and hypodermic needles to draw small quantities of the soil gas mixture for analysis in a gas chromatograph. Standard laboratory septums are used to seal the sampling ports. Gas concentrations in the head and foot spaces are sampled through the pressure port.

Column Experiments With Methane

A number of experiments on the diffusion of methane through porous media have been carried out with the soil columns. Figure 9 presents the results of two parallel experiments expressed as methane concentrations with time at the four sampling ports in the column. The gas was introduced into the head space, where the concentration stabilized at 87.6 percent for the length of the experiment. It can be seen that the gas concentration rate of change and the eventual stable concentration level is inversely proportional to the port distance from the source. In fact, 75 minutes into the experiment, the column concentrations have stabilized at what appears to be a linear concentration gradient from the head space (at 86% methane) to the foot space (at 0% methane).

The results from the first experiment are represented by the dotted lines while the symbols are from the second, parallel experiment. The replication is excellent. Figure 10 shows a comparison between the methane column experiments and simulations created through the use of the Allan Model developed earlier by this project. The comparison is excellent.

Column Experiments With Hexane

Experiments with volatile organic liquids as the vapour source required some basic modifications to the column. For hexane, the foot space was sealed off after 25 ml of liquid was in place in a foil pan. A temperature probe was inserted in the foot space to monitor the temperature range just above the liquid. The volatilization rate of hexane is temperature dependent. Therefore, the temperature readings were monitored for comparison to the measured vapour concentration with time in the foot space. A manometer was used to monitor the foot space for any pressure variation. A standard air purge, like that used in the

Figure 9: CH4 MIGRATION – EXPERIMENT 3 REPLICATION

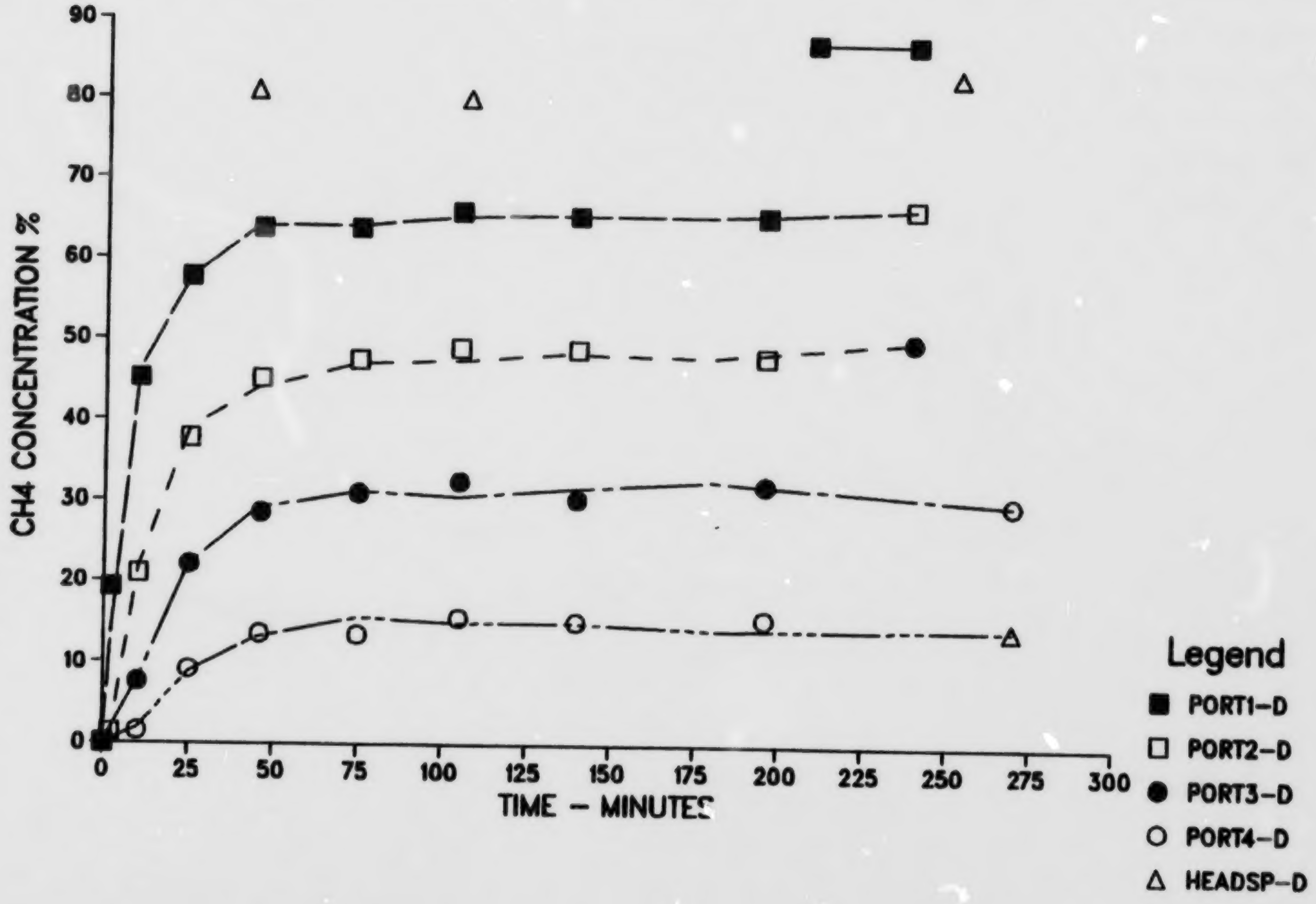
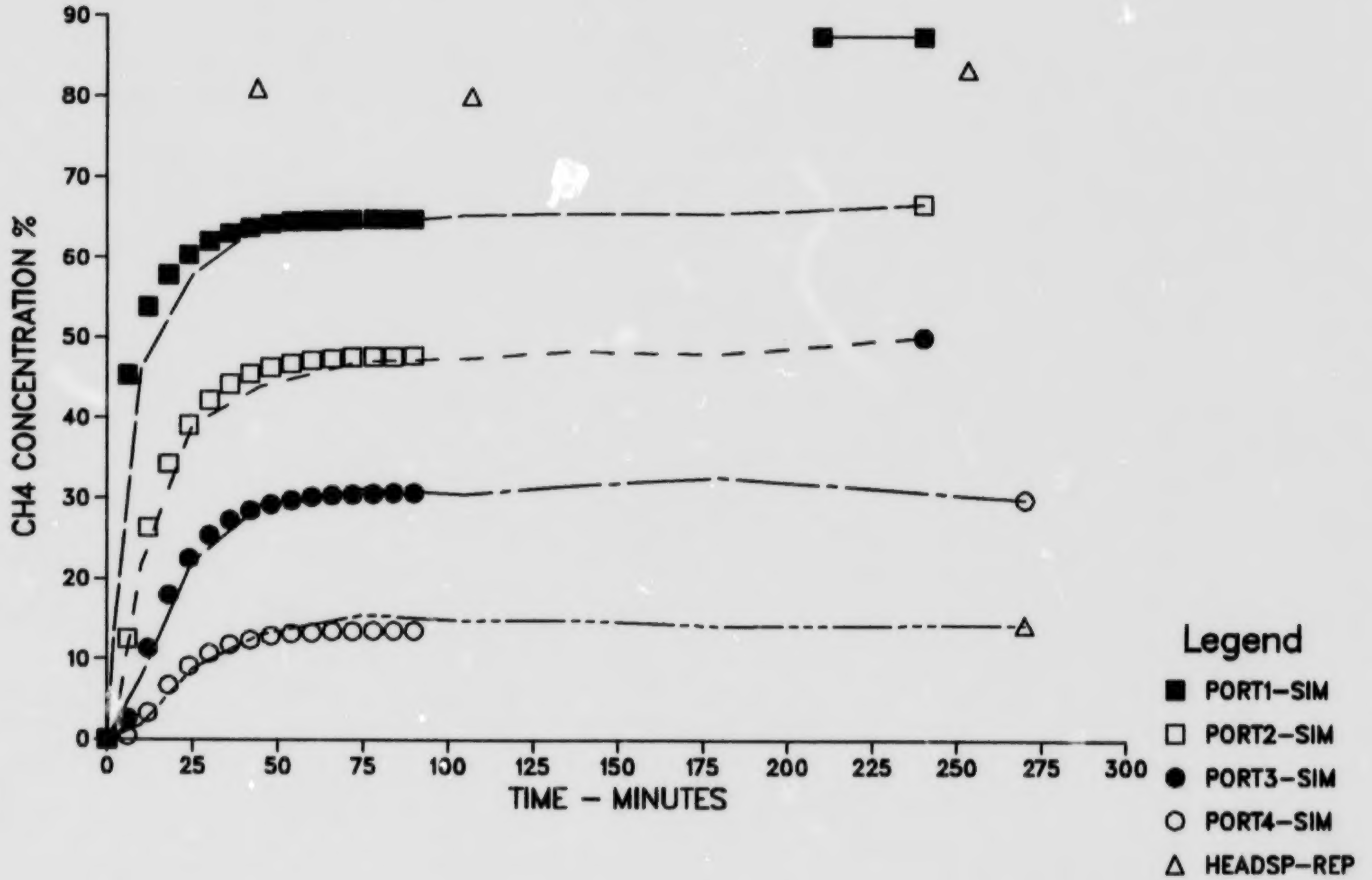


Figure 10: CH4 MIGRATION – EXPERIMENT 3 SIMULATION



82% HEADSPACE

methane column experiments, was applied to the head space to maintain an approximate zero concentration.

The results of a hexane column experiment are presented in Figure 11. The concentrations in the foot space and the sampling port nearest the source demonstrate somewhat erratic behaviour. However, this behaviour appears to be related to minor temperature fluctuations in the laboratory, resulting in significant variation in the vapour pressure of the liquid hexane.

The vapour concentrations appear to be less sensitive to head space concentration variation with distance. At ports 3 and 4, 23 and 30 cm from the source respectively, the hexane vapour concentrations showed reduced variation. The conclusion that can be drawn from this is that concentration variations recorded at the column source may be neglected for the large scale experiments such as the sandbox and in numerical modelling of vapour migration from a HIL's spill site.

A problem with condensation of hexane vapour within the sand column was anticipated and has been observed.

Column Experiments With Acetone

The results of a column experiment with acetone are presented in Figure 12. The "y" axis data are presented as a percent of the mean head space concentration (100%). For this reason, small anomalies such as head space concentration of greater than 100% were possible.

2. Flux Box Experimentation

The flux box (3.6 m long x 1.2 m high x 0.3 m wide) was designed for larger scale vapour transport experiments in soil. Source liquids can be introduced along the base of the box or within the soil at various points. Ports for sample extraction by syringe and pressure measurement exist along the sides of the box. The soil surface can be open or sealed, vegetated or stripped and quiescent or exposed to wind to study transport at this important discharge boundary.

Preliminary experiments have been conducted with methane as the source gas at the centreline of the base and Ottawa sand as the medium. Methane concentrations in the soil as % by volume after 68 and 92 minutes are shown in Figures 13 and 14 for one-half of the symmetrical box. No pressure gradient existed across the box from the source to the upper open discharge surface. The methane contours are consistent with transport by diffusion.

FIGURE 11: HEXANE MIGRATION IN COLUMN EXPERIMENT 2

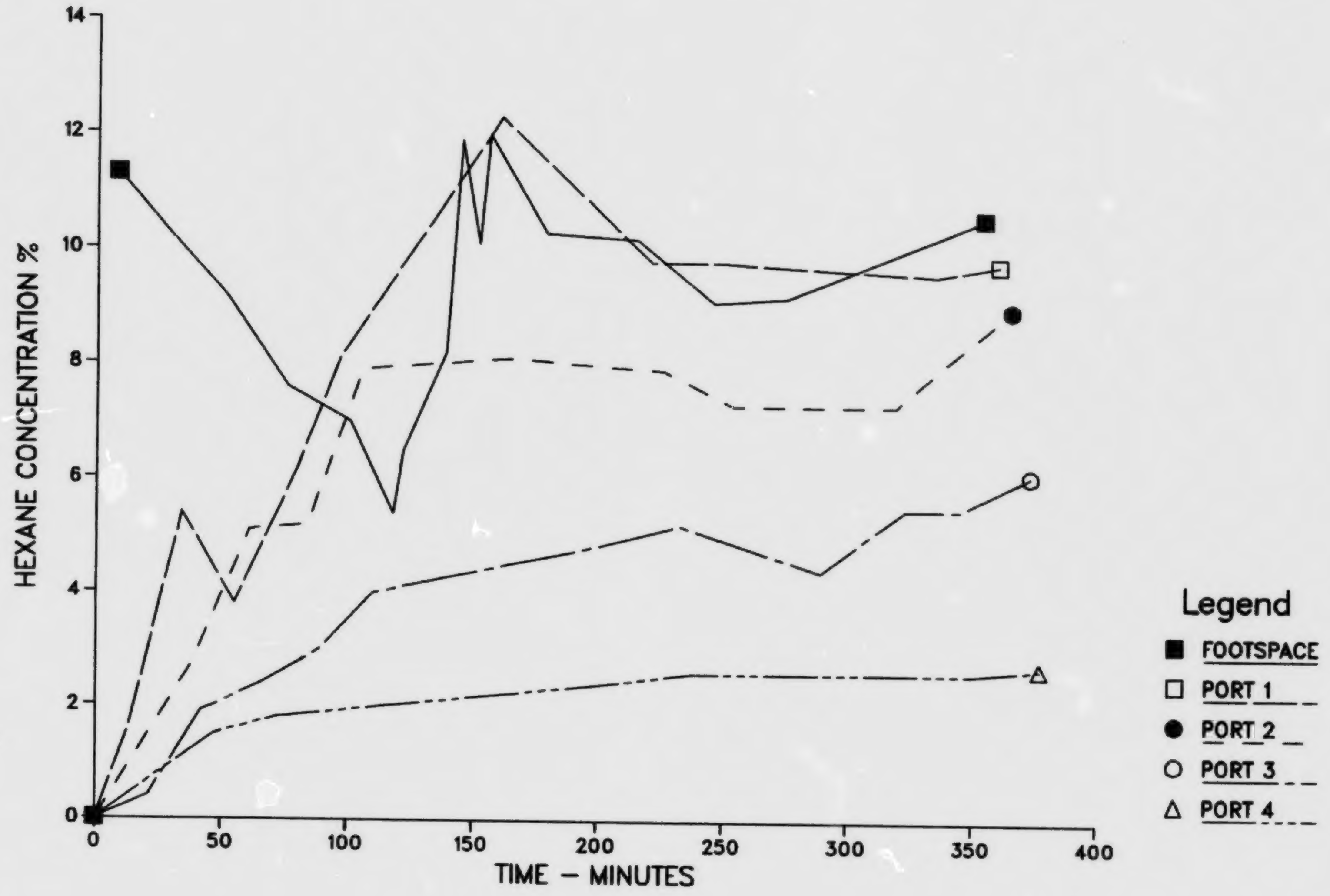
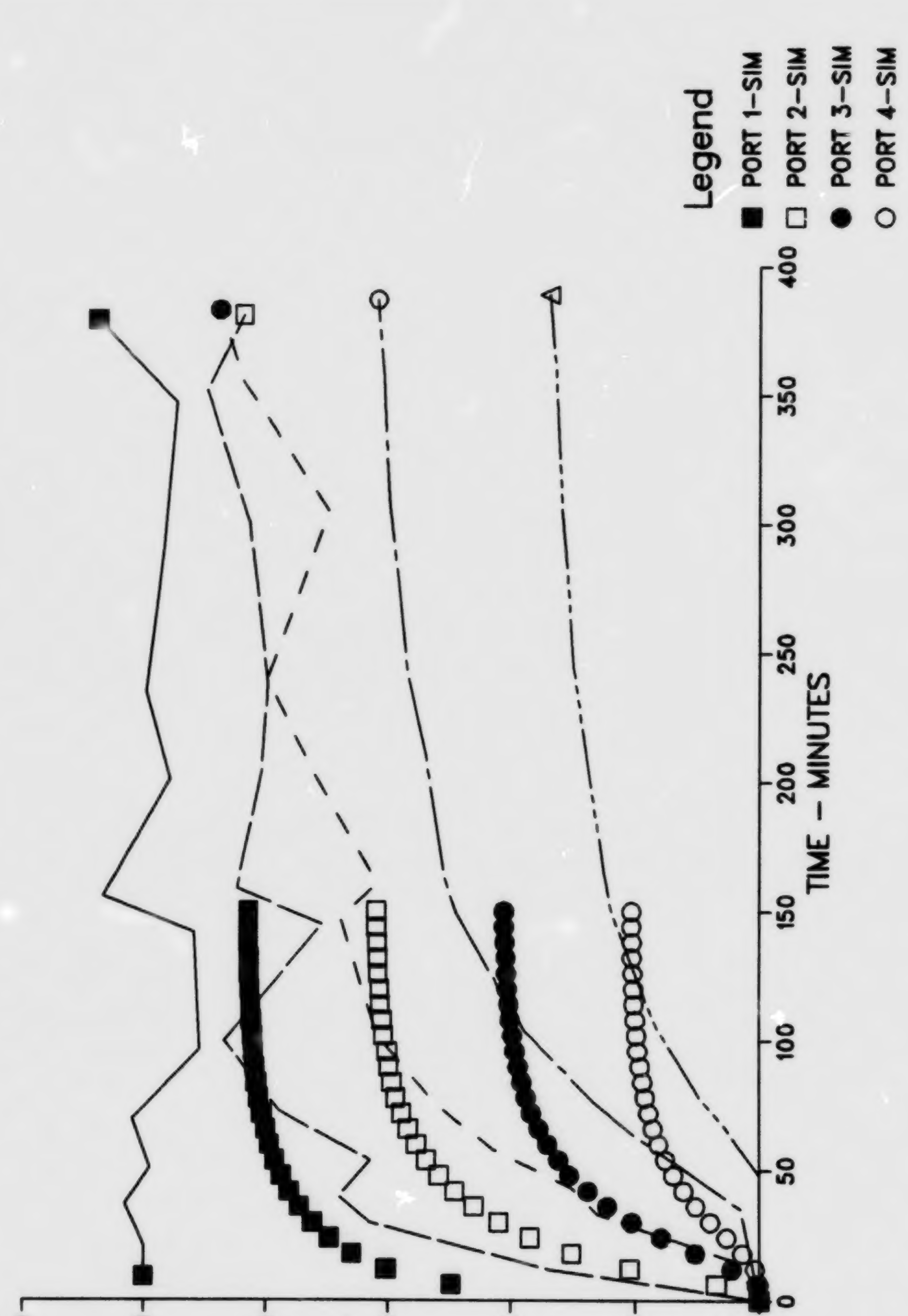


Figure 12: SIMULATION OF ACETONE COLUMN EXPERIMENT



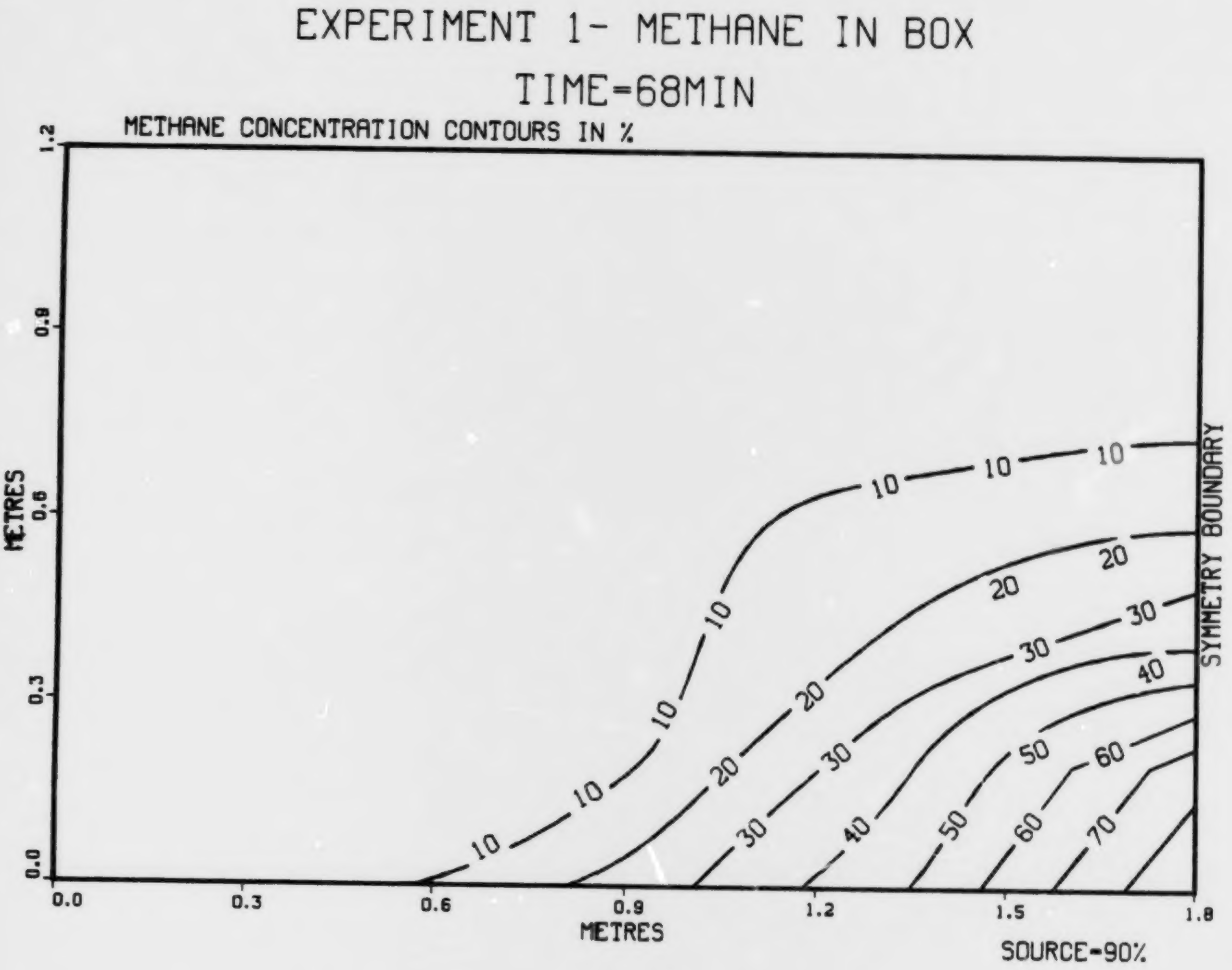

EXPERIMENT 1- METHANE IN BOX
TIME=68MIN
METHANE CONCENTRATION CONTOURS IN %
METRES
METRES
0.0
0.3
0.6
0.9
1.2
1.5
1.8
SYMMETRY BOUNDARY
SOURCE-90%
10
20
30
40
50
60
70

Figure 13

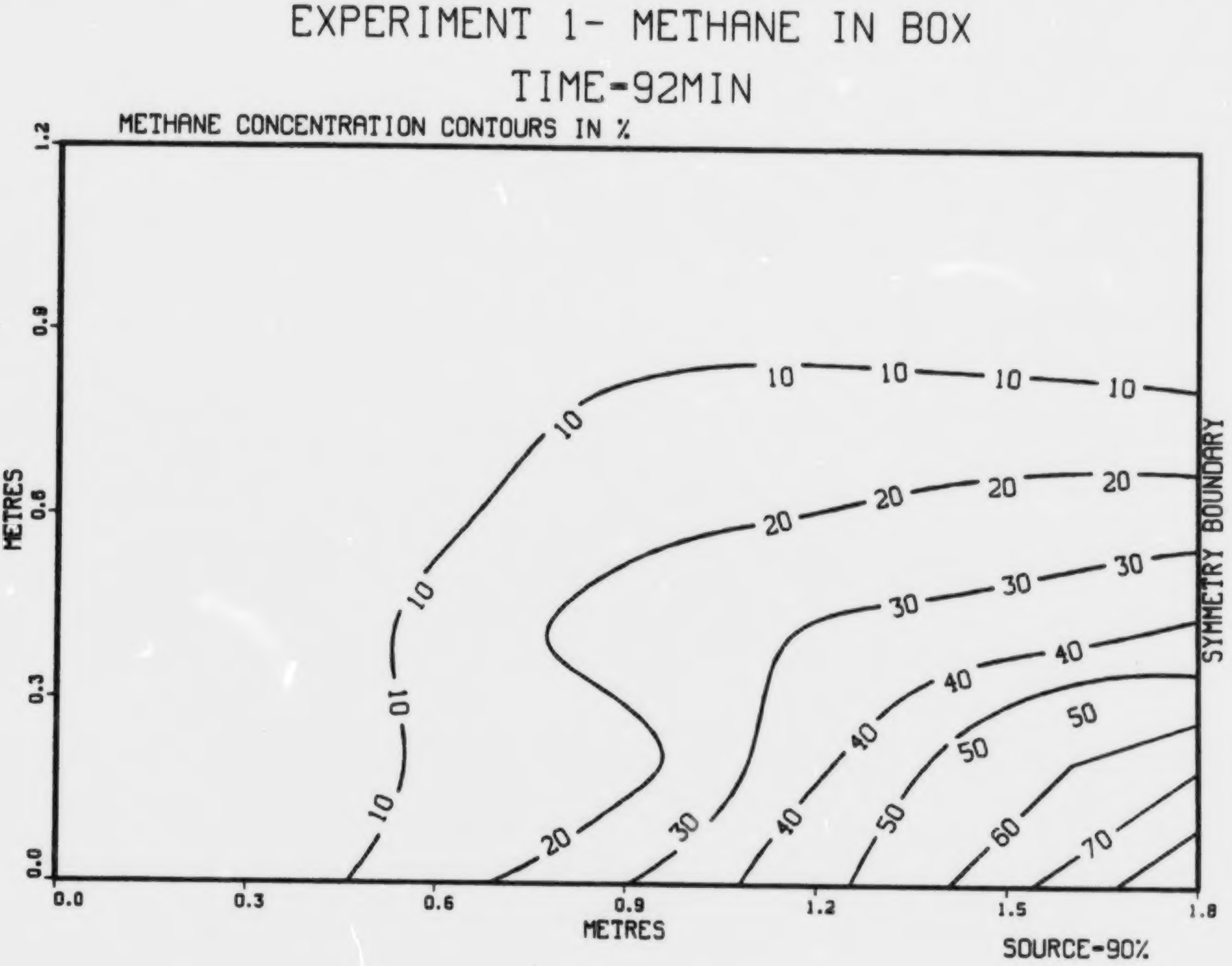

EXPERIMENT 1- METHANE IN BOX
TIME-92MIN
METHANE CONCENTRATION CONTOURS IN %
METRES
1.2
0.9
0.6
0.3
0.0
0.0
0.3
0.6
0.9
1.2
1.5
1.8
METRES
SYMMETRY BOUNDARY
SOURCE-90%
10
20
30
40
50
60
70

Figure 14

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DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

by

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DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

INTRODUCTION

Concentrated spent cyanide liquors are by-products of several different industrial processes. Although they are usually produced in relatively small quantities, their storage, transport, treatment, and disposal present considerable hazards and serious technological difficulties. Examples of spent liquors are spent cyanide solutions from electroplating and metal finishing shops, and barren bleed solutions from gold and silver extraction operations.

Concentrated cyanide solutions often accumulate in electroplating and metal finishing shops. These accumulations of 4.5 to 9.0 m^3, which may be collected over a period of years, are generally 1 to 3% cyanide, although higher concentrations may occur.

Disposal of these concentrated cyanide-containing wastewaters poses considerable problems to the waste generator. Waste haulers are often reluctant to transport these wastes because of the difficulties and expense of final disposal. Transportation of these highly toxic wastewaters involves considerable risk, as leakage or rupture of the tanker would result in a potentially lethal situation. These disposal problems are of particular concern to operators of electroplating and metal finishing shops that are usually located in highly populated urban areas. Often, the concentrated cyanide-containing wastewaters remain stored in tanks and create a hazardous situation for workers. Sometimes these wastewaters are discharged in a clandestine fashion into the municipal sewer system, creating problems downstream.

Considerable efforts have been devoted to the treatment of cyanide-containing wastewaters and several treatment technologies have been developed.

A well-known and commonly used treatment method for cyanide-containing wastewaters, particularly in the electroplating industry, is the alkaline-chlorination oxidation process which is practically applicable for wastewater containing up to 500 mg/L CN^{-2}. Other treatment processes include: peroxide oxidation; iron precipitation; ozonation with ultraviolet irradiation; carbon adsorption with catalytic oxidation; formaldehyde treatment; electrolytic oxidation; and catalytic SO_2 treatment.

Some of the common technologies available for the treatment of cyanide-containing wastewaters are not applicable to concentrated cyanide liquors. Some treatment methods are associated with high capital and operating costs, or operational complexities than render them unsuitable for small industrial plants.

A relatively new technology available for treatment of cyanide-containing wastewaters is that of polysulfide application. Polysulfide-sulfur is commercially available in a number of forms i.e. calcium polysulfide (limesulfur) or sodium polysulfide (zinc purifier). These products usually contain between 15 and 30% polysulfide-sulfur. The reaction between cyanide and polysulfide-sulfur can be simply expressed by the equation:

$$CN^- + CaS_xS \rightarrow SCN^- + CaS_{x-1}S$$

Along with the conversion of cyanide to thiocyanate, polysulfide-sulfur reacts with the metal ions present to form metal sulfides:

$$M^{++} + CaS_xS \rightarrow MS + CaS_{x-1}S$$

The required dosage of polysulfide-sulfur to convert cyanide to thiocyanate must, therefore, be greater than stoichiometric requirements (i.e. CN: poly-S^o > 1:1.23).

PREVIOUS WO[illegible]

The reaction of cyanide with polysulfide-sulfur to form thiocyanate was used as early as 1896 to remove hydrogen cyanide from coke oven gas. For cyanide solutions, the reaction was originally investigated by Wernlund and Zunick (1940). Luthy et al (1977) and Luthy and Bruce (1979) studied such transformations in coke plant and coal gasification plant effluents. International Environmental Consultants (1979 and 1981) investigated the use of the cyanide-polysulfide reaction for treatment of cyanide-containing wastewaters from the gold milling industry. However, no published data were available on the cyanide-polysulfide reaction in concentrated cyanide-containing wastewaters before the preliminary study by Takaoka and Ganczarczyk (1985). These experiments were conducted to investigate the cyanide-polysulfide reaction in a 2% solution (20,000 mg/L CN^-) of sodium cyanide. It was found that the reaction proceeded very rapidly, both at room temperature and at 3°C. It was 95% complete within 1 hour and cyanide concentrations were non-detectable within 2 weeks at a cyanide-to-polysulfide ratio of 1:2 by weight.

In a follow-up research, Ganczarczyk et al (1985) studied the cyanide-polysulfide reaction in two different wastewater streams from an electroplating operation. One wastewater was a dragout from the first rinse tank in a copper and cadmium plating process; the wastewater was a clear solution with a pH greater than 12.0. The second wastewater was a stripper solution for removal of metal plate (Cu/Ni plate stripping liquor); it was orange-red and contained a settleable yellow precipitate. The pH of the stripper solution was greater than 12.0. Sample volumes of 300-500 mL were reacted with limesulfur at cyanide to polysulfide ratios of 1:1.5 and 1:2 (w/w). Initial CN^- concentrations ranged from 11,400 mg/L to 56,200 mg/L. In each case a rapid degradation of CN^- was observed. The effective removal of CN^- occurred within 3 days for the copper/cadmium plating wastewater while

99.9% CN- removal was achieved in the copper/nickel plating wastewater within 2 days. Metal removals in these experiments were generally at the level required by municipal sewer use by-laws.

MATERIALS AND METHODS

In this work three different wastewater streams from a metal finishing shop were studied: zinc plating waste liquor (Zn/CN), cadmium plating waste liquor (Cd/CN), and copper plating waste liquor (Cu/CN). The pH in all these liquors was greater than 12.0 while cyanide concentrations ranged from 10,000 mg/L to 180,000 mg/L. A solution of potassium ferricyanide (20,000 mg/L CN) was also used to examine the effect of polysulfide on ferricyanide.

Three sources of polysulfide-sulfur were used in these experiments: limesulfur (calcium polysulfide), zinc purifier (sodium polysulfide) and calcium polysulfide produced in our laboratory from technical grade calcium oxide and sulfur. The limesulfur contained 230 g/L polysulfide-sulfur while zinc purifier contained 150 g/L and the laboratory produced polysulfide contained 200 g/L of this element.

Initial laboratory experiments were conducted in glass bottles sealed with rubber-stoppers. Later, a pilot-scale application was conducted on-site in 50 gallon drums. Samples were taken from the reactors at regular intervals, preserved and then analyzed for total cyanide (CN-), thiocyanate (SCN-) and soluble metals (cadmium, chromium, copper, iron, nickel, and zinc) contents.

The standard procedures for sample preservation were adapted from those used by Luthy et al. (1979), Luthy and Bruce (1979), and International Environmental Consultants (1981). To obtain a sample for determination of CN- or SCN-, 20 mL of the reactor contents were withdrawn in a volumetric pipette, transferred to a 200 mL volumetric flask, and diluted to the mark with distilled water. A few millilitres of a suspension of lead sub-acetate in water were added to the diluted sample to precipitate sulfides. The addition of the lead sub-acetate was stopped when the supernatant became cloudy-white, which indicated the presence of lead hydroxide. Normal sodium hydroxide solution was added to the samples in measured quantities during the sulfide precipitation process to maintain a pH range of 10 to 11. The lead sulfide precipitate was immediately separated from the sample by filtration under vacuum through a glass fiber filter. The filtrate was collected and its pH increased to greater than 11.0 with sodium hydroxide solution. The treated samples were stored in the dark at 3oC.

The method of CN- determination was adapted from the method of Knechtel and Conn as cited by Conn (1981). This method is similar to the acid reflux/distillation method in "Standard Methods" (1980) with an argentometric titration finish. The method adopted for SCN- determination was based on mercuric titrimetry after Vogel (1960), using 0.1 N mercuric sulfate. An excess of iron alum (ferric ammonium sulfate) was added to the sample under acidic conditions to produce the characteristic deep red color of ferric thiocyanate. After mercuric titration, the mercuric ion replaces the ferric ion and the red color gradually disappears, leaving the solution colorless. Polysulfides were determined with a procedure developed by Schulek as cited by Karchmer (1970). This method was based on the reaction of alkali cyanides with the soluble polysulfides under anaerobic conditions to form one SCN- ion for every atom of polysulfide-sulfur. The cyanide-polysulfide reaction was carried out in a boric acid medium. Hydrogen sulfide and excess hydrogen cyanide were driven off by boiling the acidifed solution; the SCN- and the thiosulfate remained unaffected in solution. The determination of SCN- and thiosulfate was performed by indirect iodometric titration with a starch indicator.

The analysis for soluble metals was performed using an atomic absorption spectrophotometer. A measured volume of sample filtered by a 0.45-μ membrane filter was boiled with 20 mL of concentrated nitric acid to decompose the residual cyanide that could interfere with the metals analysis. After cooling, the sample was diluted to 250 mL with distilled water and subjected to atomic absorption spectrophotometry.

EXPERIMENTAL PROGRAM AND RESULTS

The first sets of experiments were designed to determine the general effectiveness of calcium polysulfide and sodium polysulfide in the reaction with cyanide. A wastewater containing 64,900 mg/L CN- was reacted with both types of polysulfide at various CN:poly-S^o ratios. The obtained results are presented in Tables 1 and 2.

The second set of experiments involved the application of limesulfur to the three types of wastewater to determine optimum dosages and effectiveness. Results of a cyanide to polysulfide ratio of 1:2 by weight are listed in Tables 3, 4 and 5 and presented in Figures 1, 2 and 3. The results for the studied cyanide to polysulfide ratios of 1:1.5 by weight are not included in this report.

The next experiments were designed to determine the effect of dilution on the reaction of cyanide and polysulfide. Here, samples of the three wastewaters were diluted to two or three times their initial volume, and then reacted with calcium polysulfide at CN:poly-S^o ratios of 1:1.5 and 1:2 by weight. Results for dilute zinc/cyanide wastewater are listed in Table 6 and presented in Figure 4.

Table 1: Decrease of Cyanide Concentrations (mg/L) With the Application of Calcium Polysulfide As A Reagent

Ratio of CN: Poly-S (w/w)	Duration of the Experiment					
	0	0.5 hr.	1 day	2 day	3 day	4 day
1:1	64,900.0	2,125.0	2,200.0	2,437.5	2,412.5	2,050.0
1:1.5	64,900.0	125.0	75.0	12.5	25.0	0
1:2	64,900.0	12.5	12.5	0	0	0

Table 2: Decrease of Cyanide Concentrations (mg/L) with the Application of Sodium Polysulfide

Ratio of CN: Poly-S (w/w)	Duration of the Experiment					
	0	0.5 hr.	1 day	2 day	3 day	4 day
1:1	64,900.0	2,850.00	2,675.0	2,400.0	2,125.0	2,125.0
1:1.5	64,900.0	100.0	500.0	137.5	25.0	25.0
1:2	64,900.0	50.0	75.0	0	0	0

Table 3: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of Cadmium Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	65750.0	62.5	0	0	0	0
Fe	704.8	631.5	660.7	648.7	678.0	357.0
Zn	217.5	10.5	4.0	5.6	5.6	4.0
Cu	287.5	95.7	23.2	9.3	14.2	12.7
Ni	28.3	5.5	4.5	7.1	5.5	4.5
Cd	4212.5	4.5	4.7	4.0	5.3	3.2
Cr	24.8	3.0	1.0	1.3	0.5	0.5

Table 4: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of Copper Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	56075.0	62.5	0	0	0	0
Fe	416.2	485.0	396.0	452.0	425.0	356.0
Zn	2.5	0.7	0	0	0.5	1.0
Cu	35050.0	131.0	49.0	37.5	42.0	10.1
Ni	5.5	1.4	0.8	1.2	0.6	0.6
Cd	0.5	0.5	0.3	0	0	0
Cr	2.0	1.5	1.0	1.2	0.7	0

Table 5: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of X-Pert Zinc Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	7900.0	175.0	125.0	0	0	0
Fe	855.0	651.0	509.0	656.0	704.0	571.0
Zn	5325.0	132.0	2.5	3.0	1.8	2.1
Cu	6.5	2.7	0.5	0	0.3	0.5
Ni	2.5	0.8	0.4	0.6	0.4	0.4
Cd	0.5	0.3	0.3	0	0	0
Cr	4.5	2.2	0.5	0.7	0	0

It was also desired to determine the feasibility of producing calcium polysulfide on-site. Several experiments were performed in which the amounts of CaO, S, and water were varied. The reaction time was also varied. The experimental conditions and results are given in Table 7.

The final series of experiments concerned the pilot-scale application of this technology. One experiment involved the application of 20 litres of calcium polysulfide (produced in the laboratory at the University of Toronto) to 110 L of zinc/cyanide wastewater. The initial cyanide concentration was 17,900 mg/L and the polysulfide contained over 200 g/L polysulfide sulfur (CN:poly-s^o ratio of 1:2). Another pilot-scale test involved an application of 61 litres of zinc purifier containing 150 g/L polysulfide-sulfur, to 25 litres of cadmium/cyanide wastewater. The initial cyanide concentration was 181,000 mg/L (CN:poly-S^o ratio of 1:2). The results of these two experiments are presented in Tables 8 and 9 and in Figures 5, 6, 7 and 8.

Because of the apparent interference from ferricyanide (Luthy and Bruce, 1978), a series of experiments were carried out to determine the effect of polysulfide on ferricyanide. Varying amounts of sodium-polysulfide were added to a solution of potassium ferricyanide to obtain CN:poly-S^o ratios of 1:1.5, 1:2, and 1:2.5. The results are presented in Table 10.

Other work done includes:

1. Determination of the reaction heat in different spent cyanide liquors at various cyanide to polysulfide ratios.
2. Preliminary tests on the application of various reagents to remove residual polysulfide from the treated cyanide liquors after completion of the polysulfide reaction.
3. Preliminary leaching tests on the precipitates formed in the cyanide-polysulfide reaction.

The values of the reaction heat were determined by measuring the temperature rise in the laboratory reaction apparatus. In each case, 50 mL

Table 6 - Effect of Dilution on the Concentrations of Cyanide (mg/L) in the Liquid Phase with the Application of Calcium Polysuflide

Ratio of CN:Poly-S^o (w/w)	Duration of Experiments (days)					
	0	1	4	7	14	21
1:1.5	3625.0	125.0	62.5	31.3	0	0
1:2	3625.0	125.0	96.2	31.3	0	0
1:1.5	7900.0	187.5	125.0	0	0	0
1:2	7900.0	175.0	125.0	0	0	0

Table 7 - Calcium Polysulfide Production (Experimental Results and Conditions)

Sample	Components			Reaction Time (hrs)	Final Volume (mL)	Polysulfide Content
	CaO (g)	S (g)	H_2O (mL)			
1	20	70	300	24 (reflux condenser)	300	5% ± 1%
2	20	60	200	4	55	22% ± 1%
3	20	70	200	4-5	96	23% ± 1%
4	30	70	300	5	127	9% ± 1%
5	20	60	400	7	130	16% ± 1%

* Note: all samples were continually stirred throughout boiling time with a magnetic stirrer.

Table 8 - Liquid Phase Pollutant Concentrations (mg/L) in the Treatment of Zinc/Cyanide Spent Liquor (initial cyanide to polysulfide ratio of 1:2)

Pollutants	Duration of Experiments (days)						
	Initial	1	3	6	13	23	30
CN	17900.0	1125.0	425.0	225.0	100.0	300.0	350.0
SCN	0.0	21140.0	12550.0	11620.0	4650.0	11620.0	6970.0
Fe	2600.0	220.0	140.0	100.0	120.0	120.0	120.0
Zn	9000.0	140.0	540.0	20.0	20.0	20.0	16.0
Cu	50.0	8.0	10.0	6.0	4.0	2.0	0.0
Cd	0.3	0.0	0.0	0.0	0.0	0.0	0.0
Cr	5.0	5.0	4.0	4.0	2.0	2.0	2.0
Ni	20.0	12.0	20.0	14.0	2.0	2.0	2.0

Table 9 - Liquid Phase Pollutant Concentrations (mg/L) in the Treatment of Cadmium/Cyanide Spent Liquor (initial cyanide to polysulfide ratio of 1:2)

Pollutants	Duration of Experiments (days)					
	Initial	1	3	6	9	16
CN	181000.0	63.0	10.0	15.0	12.5	10.0
SCN	0.0	6970.0	3950.0	1160.0	2556.0	860.0
Fe	1400.0	6.2	2.5	0.8	2.0	1.9
Zn	940.0	0.6	0.6	0.7	2.0	0.8
Cu	660.0	0.8	1.0	1.1	1.2	0.6
Cd	9800.3	0.4	0.3	0.5	0.4	0.3
Cr	15.0	2.0	3.1	2.4	2.8	1.6
Ni	36.0	3.8	3.0	2.4	1.8	1.4

Table 10 - Concentration of Pollutants (mg/L) in the Liquid Phase Obtained During Treatment of Potassium Ferricyanide with Sodium Polysulfide

No.	Ratio of CN:poly-S^o (w/w)	Pollutants (mg/L)	Duration of Experiments (days)			
			0	1	3	9
1	1:1.5	CN	20000	12000	10200	7750
		Fe	7155	3000	1800	1000
		SCN	0	0	0	0
2	1:2	CN	20000	7800	5000	8750
		Fe	7155	800	600	1400
		SCN	0	0	0	0
3	1:2.5	CN	20000	9500	1700	2250
		Fe	7155	1000	800	400
		SCN	0	0	0	0
4	1:2	CN	200	163	nd	125
		Fe	72	26	nd	20
		SCN	0	0	nd	0

*note: nd = not done

Table 11 - Estimation of Reaction Heat

Sample Source	Cyanide Amount (g)	Initial CN:Poly-S^{0}	Initial Temperature (^{0}C)	Peak Temperature (^{0}C)	Maximum Temp. Rise (^{0}C)	Heat of Reaction (cal/g (CN)
Zinc-Plating Solution	0.3500	1:1.5	27.49	30.36	2.87	410.0
		1:2	28.27	31.24	2.97	424.3
Cadmium-Plating Solution	0.6103	1:1.5	25.86	30.83	4.97	407.2
		1:2	26.80	31.96	5.16	422.7
Copper-Plating Solution	1.1719	1:1.5	26.67	31.79	5.12	218.4
		1:2	25.80	31.14	5.34	227.8
Copper-Plating Solution	0.9354	1:1.5	26.50	30.00	3.50	187.1
	2.8013		26.80	36.30	9.50	169.6
KCN Solution	0.2000	1:2	27.04	28.70	1.66	415.0
			27.01	28.73	1.72	430.0

* Specific heat of these solution is assumed to be 1 cal/g.^{0}C.

Table 12 - Removal of Excess Polysulfide from the Cadmium Electroplating Solution

Test No.	1	2	3	4	5
Volume of Sample (mL)	10	10	10	10	10
Volume of 10% $FeSO_4 \cdot 7H_2O$ sol. Added (mL)	0	1	3	4	5
Poly-S^o concentration (mg/L)	10740.1	4618.2	961.8	480.9	705.3
Removal Efficiency (%)	0	43	91	95.9	93.4

Table 13 - Metal Ion Concentrations in the Leachate from the Zinc Electroplating Solution Precipitate (mg/L)

		Duration of Leaching				
		1 day	3 day	7 day	9 day	15 day
Fe	A	nd	nd	14.0	6.8	13.0
	B	nd	nd	11.6	4.6	11.2
Zn	A	nd	0	0.2	0	0
	B	nd	6.6	5.1	0	4.8
Cu	A	nd	nd	0.8	1.0	0.8
	B	nd	nd	0.6	1.0	0.6
Ni	A	nd	nd	0.4	0	0
	B	nd	nd	0.2	0.2	0
Cd	A	nd	nd	0	0	0
	B	nd	nd	0	0	0
Cr	A	nd	nd	0	0	0
	B	nd	nd	0	0	0

Note:
A represents the sample of precipitate + fly ash
B represents the sample of precipitate only
nd: not done

Table 14 - Metal Ion Concentrations in the Leachate from the Copper Electroplating Solution Precipitate (mg/L)

		Duration of leaching		
		1 day	3 day	9 day
Fe	A	0.6	0	0.8
	B	0.2	0.2	0.8
Zn	A	0.2	0.4	0.4
	B	0.2	0.2	0.2
Cu	A	2.6	2.0	0.6
	B	1.0	1.0	0.8
Ni	A	0.4	0.2	0.2
	B	0.4	0.4	0
Cd	A	0	0	0
	B	0	0	0
Cr	A	0	0	0
	B	0	0	0

Note: A represents the sample of precipitate + fly ash
B represents the sample of precipitate only

Table 15 - Metal Ion Concentrations in the Leachate from the Cadmium Electroplating Solution Precipitate (mg/L)

		Duration of leaching		
		1 day	3 day	9 day
Fe	A	9.6	6.8	6.6
	B	6.0	4.6	4.0
Zn	A	0.2	0	0
	B	0.2	0	0
Cu	A	0.8	1.0	0.8
	B	0.8	1.0	0.8
Ni	A	0.6	0	0.4
	B	0.8	0.2	0.6
Cd	A	0	0	0
	B	0.2	0	0
Cr	A	0	0	0
	B	0	0	0

Note: A represents the sample of precipitate + fly ash
B represents the sample of precipitate only

samples were used, and the reactor was continually agitated to ensure a uniform temperature distribution throughout the vessel. The obtained data are listed in Table 11.

Removal of residual polysulfide from the treated liquors by the additions of $FeSO_4$ was examined by taking 10 mL samples of the cadmium/cyanide-polysulfide reaction product and adding to it 1, 3, 4, 5, 7 and 10 mL of 10% $FeSO_4 \cdot 7H_2O$. The resulting data are presented in Table 12.

The procedure employed in the precipitate leaching tests was as follows: The precipitate was first dried in an oven at 103°C. One gram of the dried precipitate was added to 100 mL of distilled water. To some samples, 1 g of fly ash was also added in a slurry of its original solution. All samples were then shaken, and dissolved metals concentrations were determined at regular intervals. The results are presented in Tables 13, 14 and 15.

DISCUSSION

There was no significant difference in efficiency between calcium polysulfide and sodium polysulfide applied for cyanide liquors treatment. Both types of polysulfide were effective at reducing cyanide concentrations at cyanide to polysulfide ratios of 1:2 and 1:1.5. Because calcium polysulfide could be presumably cheaper if produced in bulk quantities, it was chosen as the preferred alternative. A preliminary economic analysis revealed that calcium polysulfide could be produced at 40% of the purchase cost. Current prices for limesulfur (bulk) are $1.50/Litre @ 230 g/L polysulfide sulfur. Zinc purifier is available for $1.05/Litre, but it contains only 150 g/L polysulfide sulfur. So, for 1 kg polysulfide sulfur (for example) the costs are as follows:

Limesulfur (calcium polysulfide):	4.3 L @ $1.50/L = $6.53
Zinc Purifier (sodium polysulfide):	6.67 L @ $1.05/L = $7.00

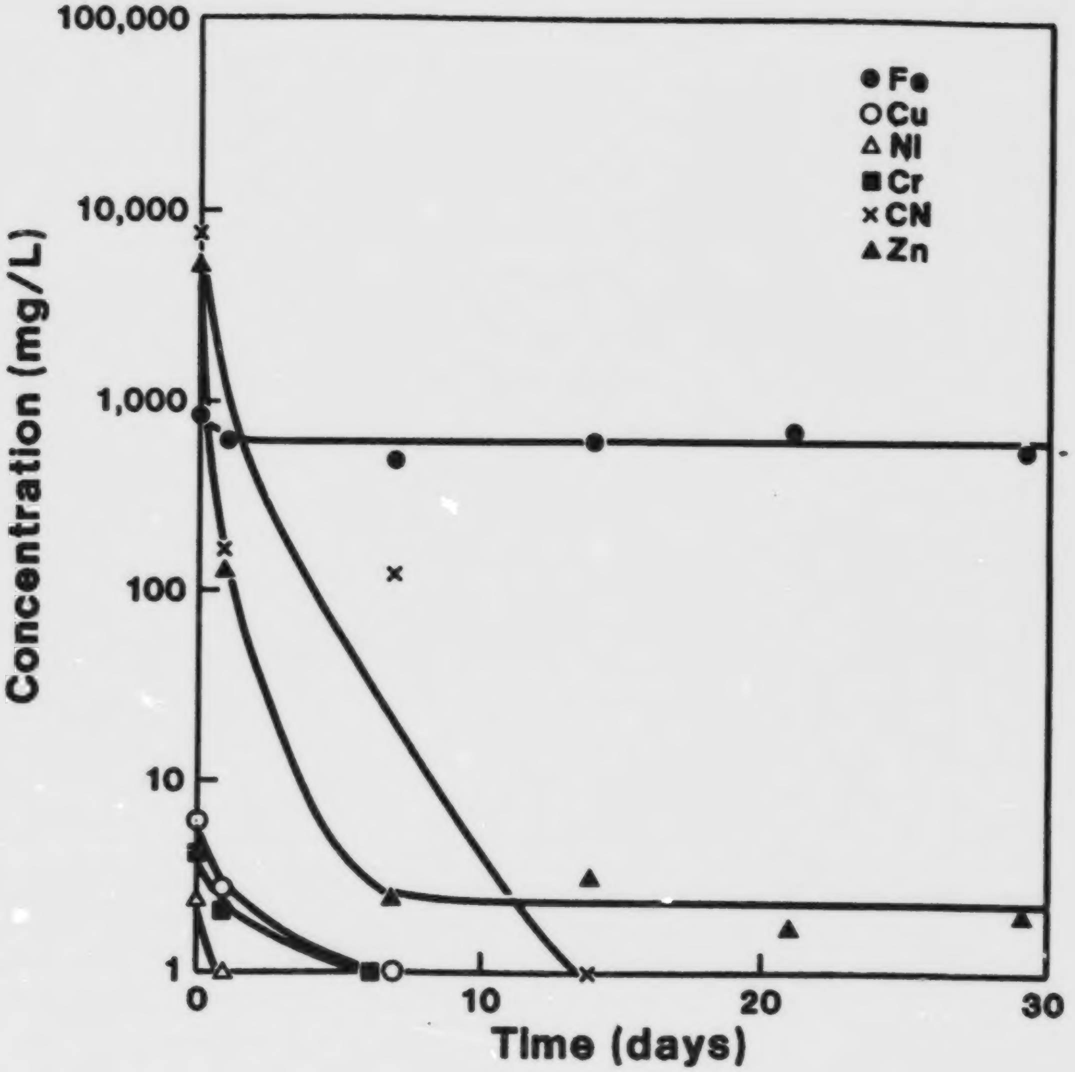

Figure 1 - Application of calcium polysulfide in the treatment of a Zinc/Cyanide spent liquor at a CN:Poly-So Ratio of 1:2.

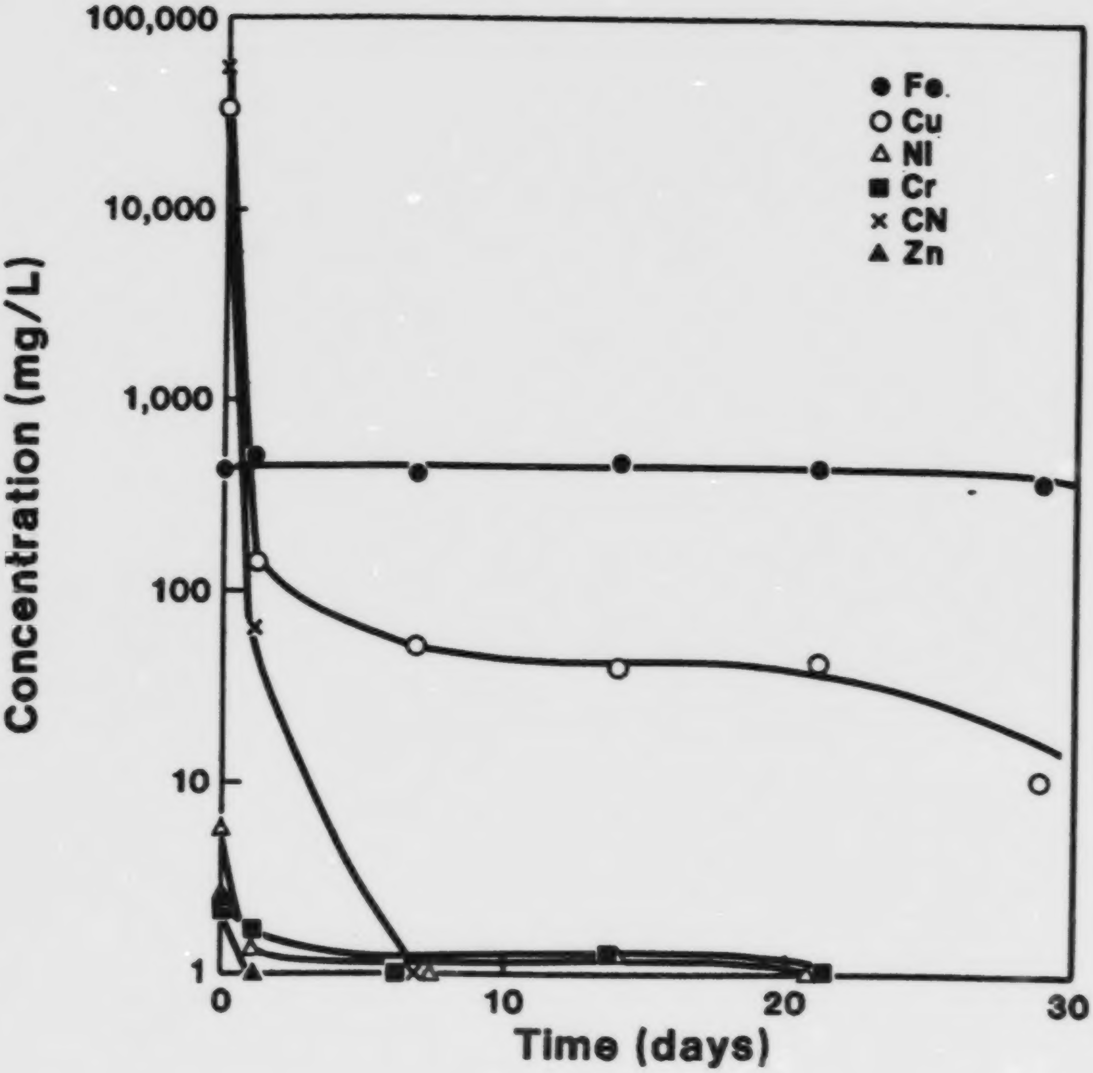

Figure 2 - Application of calcium polysulfide in the treatment of a Copper/Cyanide spent liquor at a CN:Poly-S° ratio of 1.2.

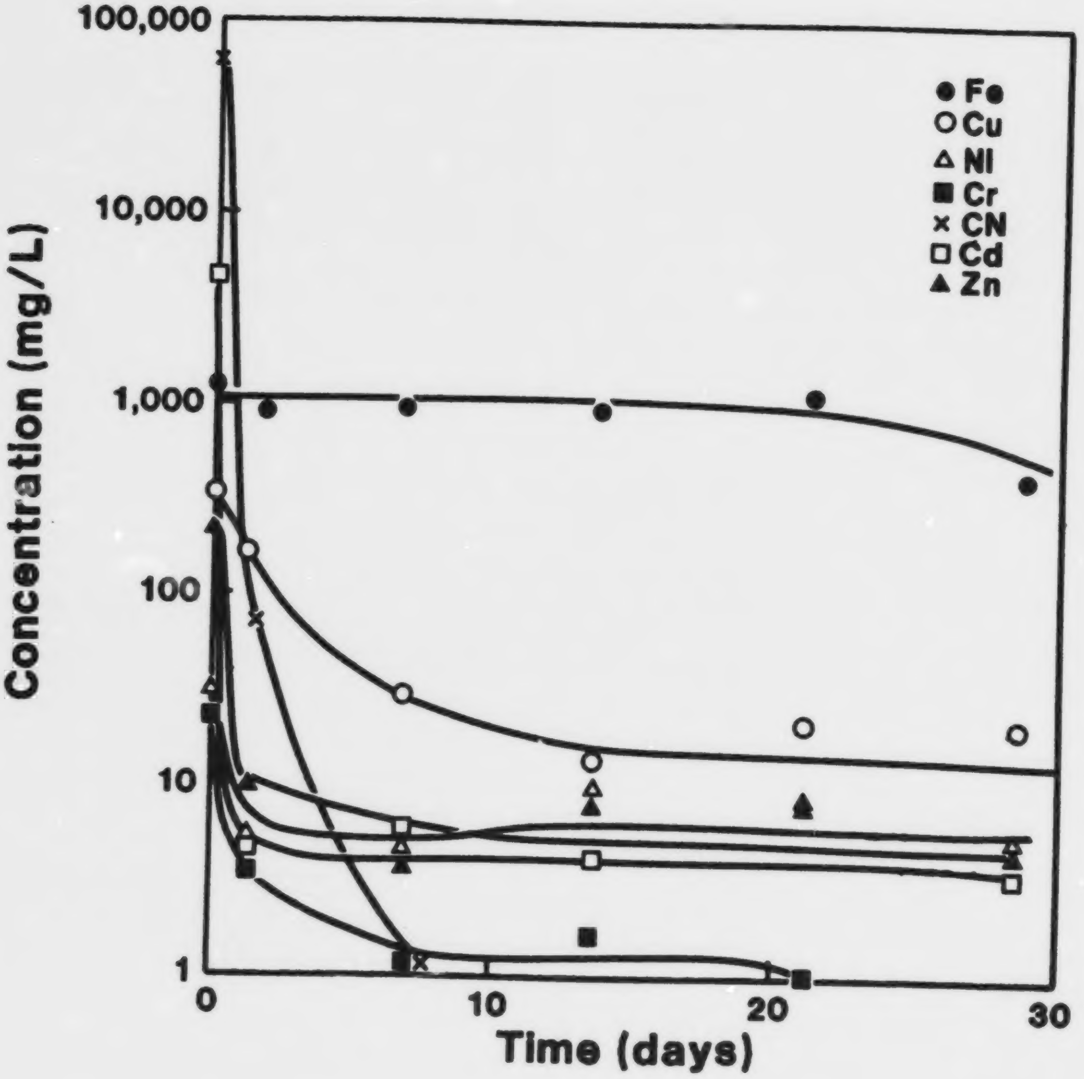

Figure 3 - Application of calcium polysulfide in the treatment of a Cadmium/Cyanide spent liquor at a CN:Poly-So ratio of 1:2.

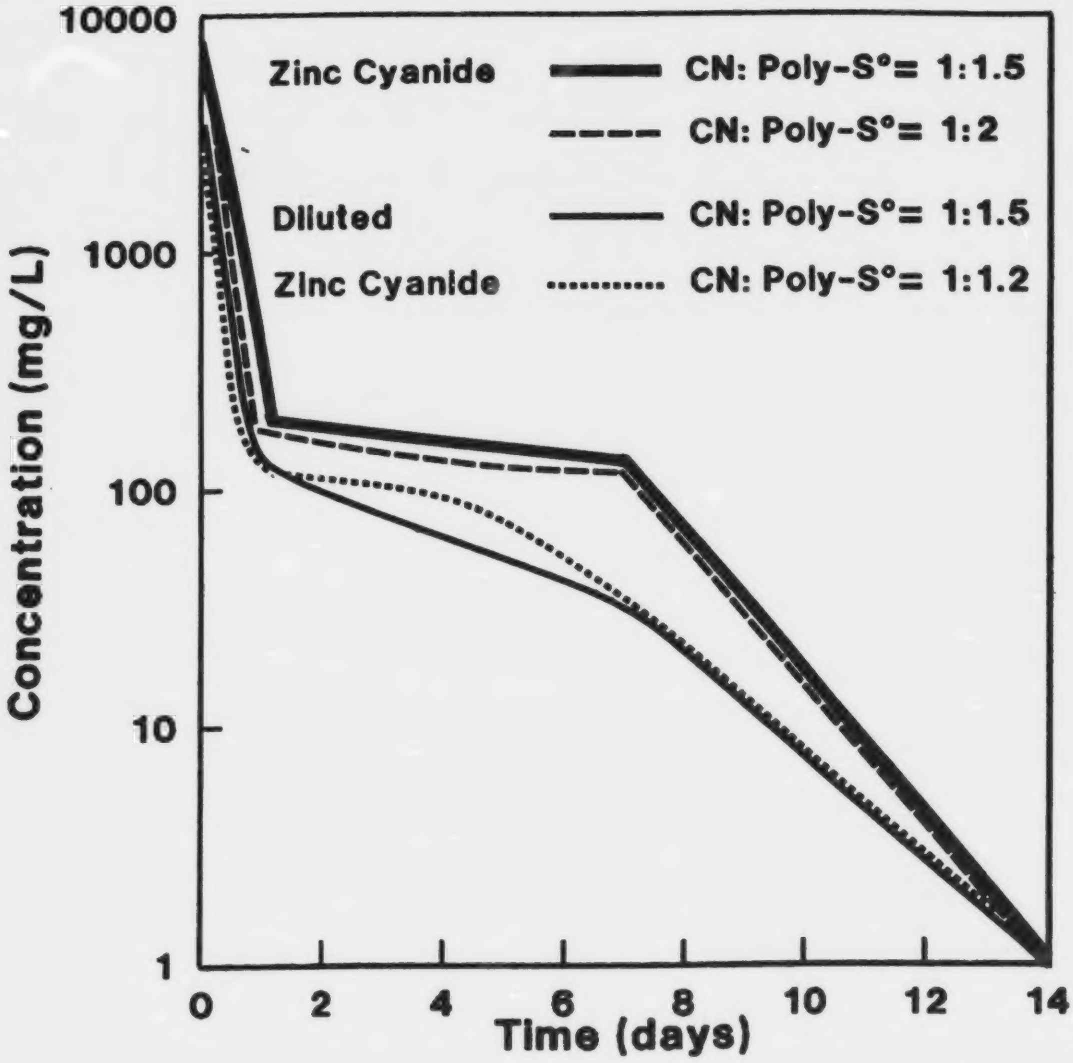

Figure 4 - Effect of dilution on cyanide removal by the Application of calcium polysulfide.

It must be noted, however, that zinc purifier is readily available at most metal finishing shops since it is commonly used in day-to-day operation as a plating bath purifier.

The preliminary tests on the three studied wastewaters showed rapid degradation of CN-. Cyanide was reduced to non-detectable levels within 7 days for both the cadmium/cyanide and copper/cyanide wastewaters at cyanide to polysulfide ratios of 1:2. The zinc/cyanide wastewater required two weeks to bring the cyanide levels to the non-detectable range i.e. < 1 mg/L.

Metal ion removal was also quite effective in all cases. Most metals were reduced to concentrations less than 10 mg/L (after 28 days) with the exception of iron and copper. However, the eventual copper levels were only slightly above 10 mg/L for the cadmium/cyanide and copper/cyanide wastewaters. But the iron content remained at concentrations above 350 mg/L in all the studied cases. In the zinc/cyanide wastewater, iron remained at a concentration of 570 mg/L. It appears that iron, while being difficult to remove, also hinders the cyanide-polysulfide reaction. This hypothesis was further substantiated by the pilot-scale application results.

Dilution did not have a significant effect on the cyanide-polysulfide reaction. After 1 day, 96.5% of the cyanide was removed in the diluted sample, while 97.6% was removed in the undiluted sample. The diluted sample did, however, take longer to reach undetectable cyanide concentrations.

Experiments showed that calcium polysulfide can be produced by the user. Concentrations as high as 23% polysulfide-sulfur were attained after 4-5 hours of boiling the lime suspension with elemental sulfur. Based on these results, 20 litres of 20% calcium polysulfide were produced in the laboratory at the University of Toronto. This was then used to treat 110 litres of zinc/cyanide wastewater in the first pilot-scale test (see Figures 7 and 8).

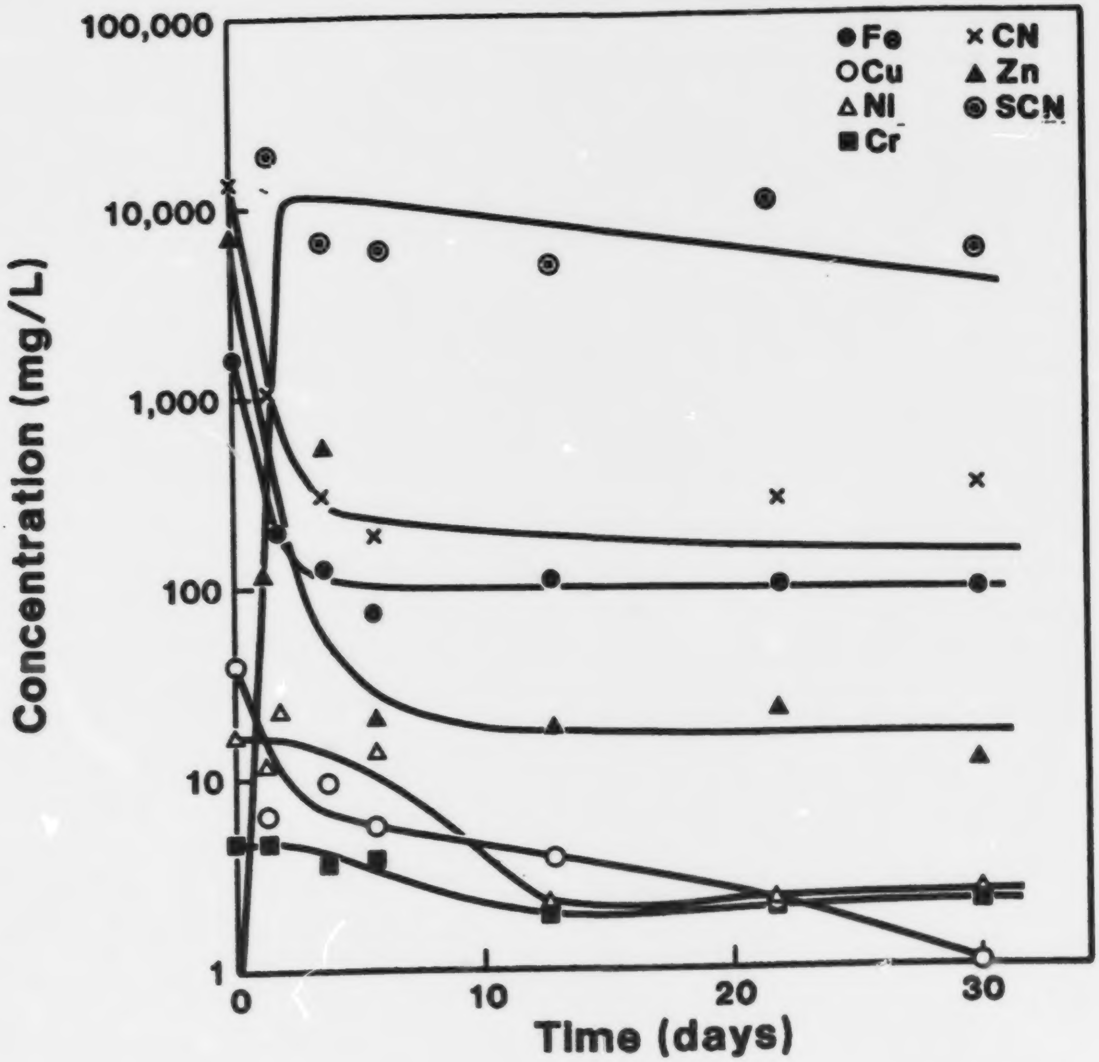

Figure 5 - Pilot-Scale application of produced calcium polysulfide in the treatment of Zinc/Cyanide spent liquor at a CN:Poly-S^o ratio of 1:2.

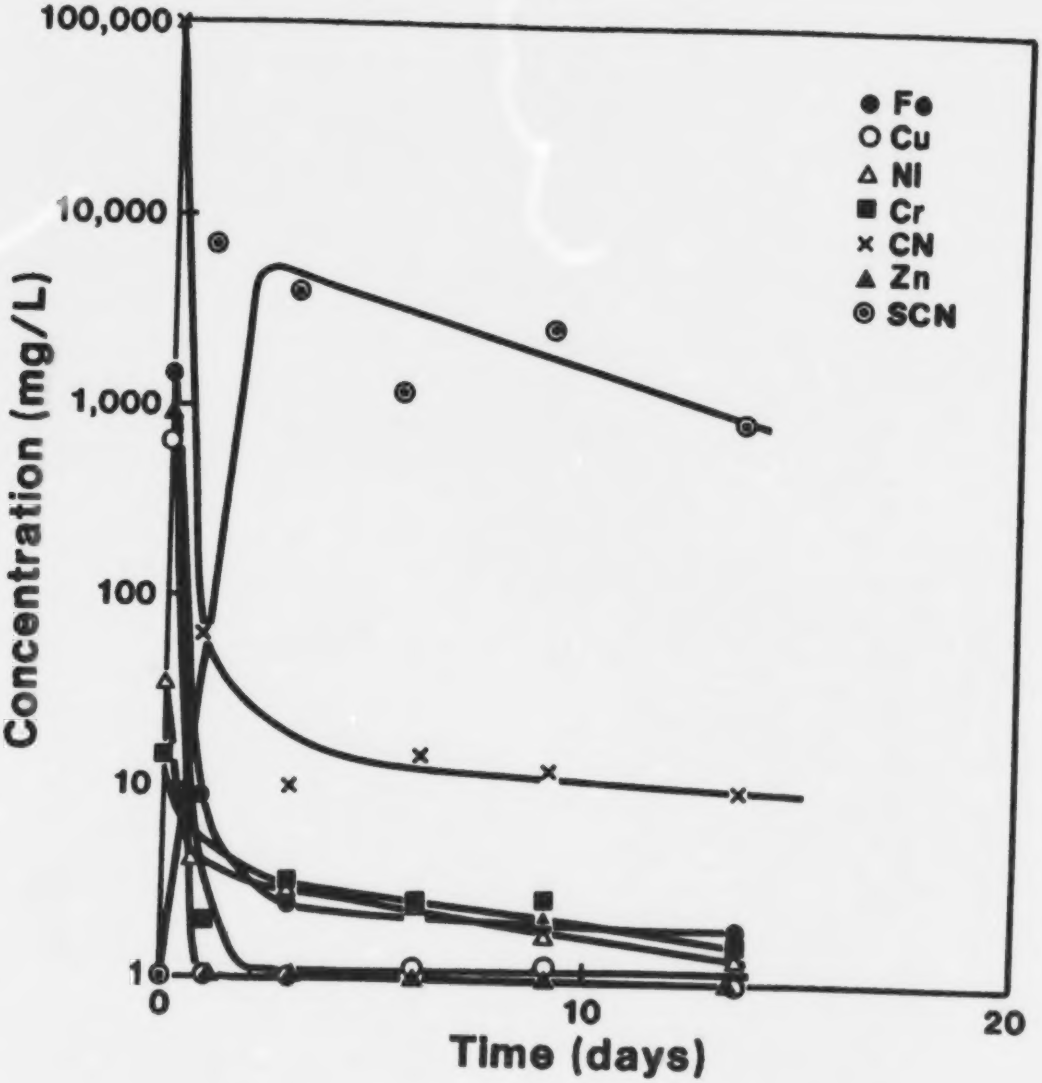

Figure 6 - Pilot-Scale application of purchased sodium polysulfide in the treatment of Cadmium/Cyanide spent liquor at a CN:Poly-So ratio of 1:2.

Figure 7 - Reaction of Zinc/Cyanide Wastewater with Produced Calcium Polysulfide.

Figure 8 - Reaction Vessel Used in Pilot-Scale Application of Polysulfide.

Cyanide concentrations were reduced by 97.6% within 3 days. A slight decrease over the next few weeks was observed but complete removal was not attained. It was hypothesized that this was due to the high initial iron concentrations. This was somewhat substantiated by the second pilot-scale test. Along with the decreasing cyanide concentrations, an initial thiocyanate increase was noted. As it was observed by Ganczarczyk et al (1985), the thiocyanate concentration then decreased over the duration of the test.

As with the preliminary tests, most metals were reduced to concentrations below 10 mg/L. The exceptions here were Zn and Fe. The lowest zinc concentrations were determined at 16 mg/L, while iron content remained steady at 120 mg/L. Considering the very high initial iron concentration (2600 mg/L) the iron removal achieved was quite good. It was postulated that perhaps a further addition of polysulfide might take the reaction to completion. This was not found to be the case, however. Experiments not cited here revealed that no additional cyanide removal had taken place.

The second pilot-scale application of polysulfide was somewhat more successful than the first one. Cyanide concentrations were reduced by 99.9% after one day. As with the first test, cyanide concentrations could not be brought down to undetectable levels. Thiocyanate also displayed similar characteristics to those in the first test, i.e. initial increase followed by a continual decrease. The peak thiocyanate concentrations were, however, considerably less (7,000 mg/L vs 21,000 mg/L). A temperature rise of 12°C was noted at the beginning of the experiment.

Metal ion removal was considerably more effective in the second pilot-scale test. All metals (including iron) were brought to concentrations less than 5 mg/L within 10 days. The initial iron concentration, however, was much lower in the second test (1,400 mg/L vs 2,600 mg/L). This increased removal in the cadmium/cyanide wastewater (compared to the zinc/cyanide wastewater) was, however, not unexpected. The initial tests also showed some difficulty in dealing with the zinc/cyanide wastewater. As it was mentioned earlier in the discussion, it was hypothesized that the differences in removal efficiencies may have been due to the iron concentrations.

To further examine this possibility, the potassium ferricyanide-polysulfide tests were conducted. In all cases, cyanide concentrations were reduced but no thiocyanate was formed in this reaction. This further confirms the results of Luthy & Bruce (1978). It seems that some further cyanide-metal complexation occurs with the addition of polysulfide. No further tests were done on this phenomenon.

The values of the reaction heat for both the zinc/cyanide and cadmium/cyanide wastewaters were found to be about 400 cal/g (CN). The temperature rise in the mixture thus depends on the amount of cyanide present. In the second pilot-scale test, a rise of 12°C (from 27°C to 39°C) was noted at the beginning of the test. Considering that the initial cyanide concentration was 181,000 mg/L, however, no problems in this regard are foreseen.

Since polysulfide is known as a very active substance, it may cause problems to the receiving water body if discharged without further treatment. Removal of residual polysulfide is therefore of some concern. Experiments showed that the addition of $FeSO_4$ can effectively remove residual polysulfide. Since $FeSO_4$ is usually readily available in metal finishing shops (i.e. it is produced in the recovery of sulfuric acid from spent pickle liquors), the process itself is inexpensive. The procedure also results in a decrease in pH which makes the effluent easier to discharge.

The preliminary leaching tests on the precipitates show that the metal ion concentrations in the leachate are quite low. This is primarily due to the very low solubilities of metal sulfides. The addition of flyash reduced the metal ion concentrations in some instances. This is attributed to the sorption capacity and ion exchange capability of the flyash. Further tests on the precipitates formed in the cyanide-polysulfide reaction are planned.

CONCLUSIONS

This study was conducted to examine the effectiveness of the cyanide-polysulfide reaction in treating concentrated cyanide liquors that contained soluble metal compounds presumably in the form of metal-cyanide complexes. The primary objective was to produce an effluent acceptable for discharge to municipal sanitary sewer systems. Although many questions of scientific interest were left to be resolved, the following conclusions were made:

- There is effectively no difference between calcium and sodium polysulfide as a reagent for this treatment.
- Dilution has little effect on cyanide and metal ion removals; the reaction is actually more rapid at higher cyanide cincentrations.
- Calcium polysulfide can be easily produced on-site at practical ranges of concentration.
- Over 95% of cyanide can be effectively removed from concentrated spent liquors with the addition of polysulfide at CN:poly-S^o ratios only slightly greater than stoichiometric requirements (i.e.> 1:1.23).
- Metals can be reduced to concentrations of less than 10 mg/L with the exception of iron when it is present in very high initial concentrations.

- SCN- produced by CN- conversion was partially lost during the process.
- Polysulfide does reduce cyanide concentrations in ferricyanide but does not form thiocyanate in this reaction.
- The cyanide/polysulfide reaction is mildly exothermic (about 400 cal/g CN).
- Residual polysulfide is easily removed from the reaction product by the addition of $FeSO_4$. Removal efficiencies are greater than 95%.
- Very little metal ion leaching can be expected from the precipitate formed in the reaction between cyanide liquors and polysulfide.

It is believed that the cyanide-polysulfide reaction provides a safe, effective, and practical means of detoxifying highly concentrated waste cyanide solutions. The simplicity of the process and the ready availability of the polysulfide reagent make this technology appropriate for use in some small electropolating shops or developing countries.

Treatment of Landfill Leachate By Spray Irrigation - Muskoka Lakes

R.A. McBride[1] A.M. Gordon[2] P.H. Groenevelt[1]

Introduction

The Muskoka Lakes sanitary landfill site (lots 21, 22 and 23, Concession 1, Medora Ward, Township of Muskoka Lakes, District Municipality of Muskoka) is the first known location in Ontario to have installed a leachate collection and spray irrigation disposal facility. The system at the present time consists of i) a leachate collection trench situated downslope from the capped landfill, ii) two settling lagoons where some limited aeration treatment is achieved, and iii) a network of 72 spray irrigation nozzles distributing partially treated leachate over three areas totalling approximately 4.3 ha in a mixed hardwood forest (see Figure 1). Spray irrigation was selected as an engineering solution to the leachate generation problem of this site since a suitable alternative disposal site for source removal though excavation and transport could not be found within the municipality (M.M. Dillon, 1980; Totten, Sims, Hubicki Assoc. Ltd., 1983).

At current rates, $2.4 \times 10^{7}\ \ell$ or more of leachate will be generated and collected annually at this landfill for decades to come. Given the maximum current disposal capacity of about $2.0 \times 10^{7}\ \ell \cdot yr^{-1}$ under ideal conditions between April and October at this site (i.e. spraying not abated due to rainfall), even the current scale of operations may provide inadequate over the long-term (Gartner Lee Assoc. Ltd., 1984). Little published research exists on leachate disposal and attenuation through spray irrigation on land which is applicable to Ontario conditions. This would suggest that unforeseen problems may arise in the future which would preclude leachate application at the present rates and reduce the efficiency and acceptability of this disposal method in both economic and environmental terms.

A one year research study was initiated in 1986, with the financial support of the Ontario Ministry of the Environment, which constitutes the first phase of a longer term (3 year) research plan on this method of leachate disposal in Ontario. Consistent with the above concerns, the broad study objective is to evaluate leachate spray irrigation as a cost-

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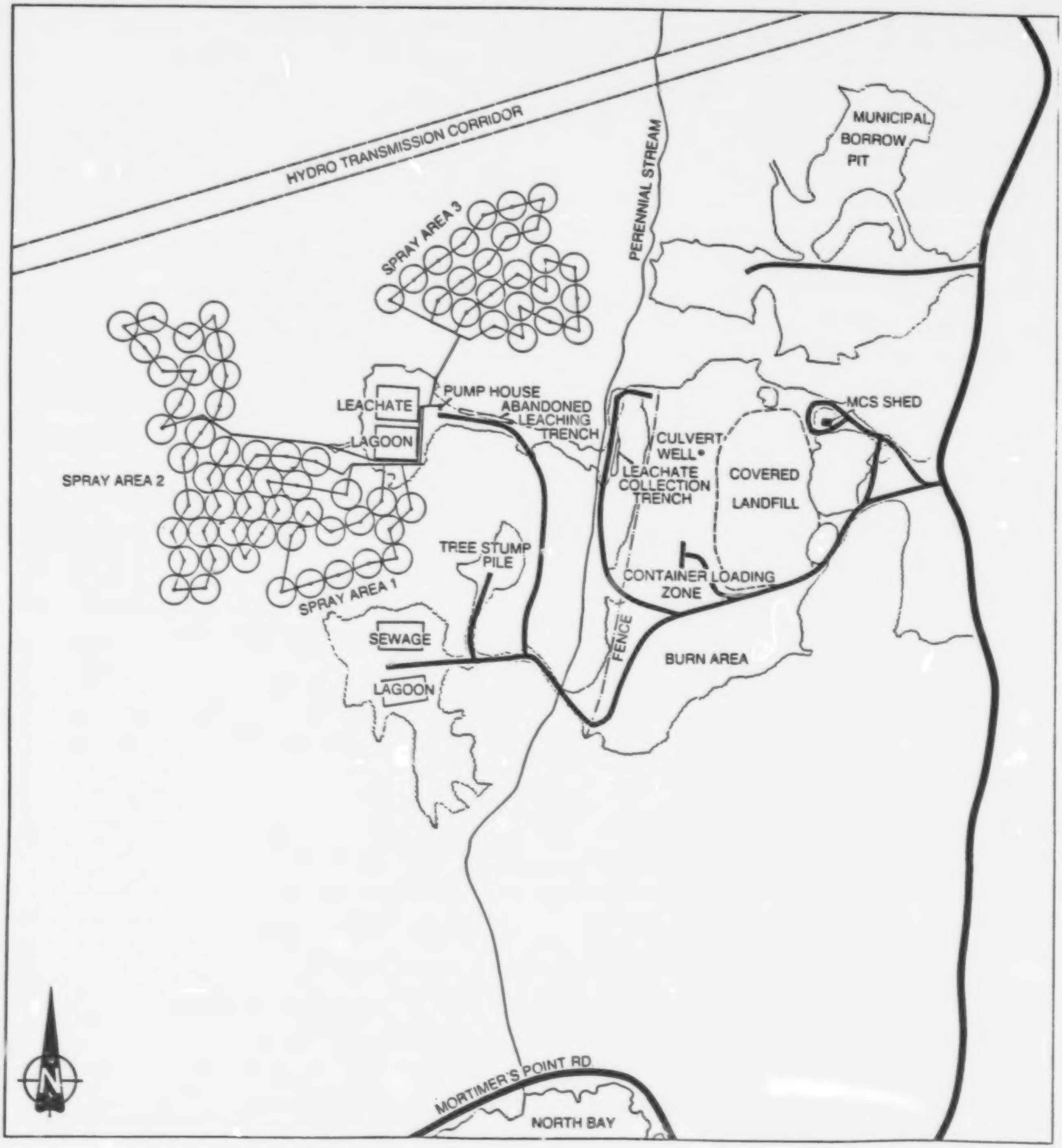
HYDRO TRANSMISSION CORRIDOR
PERENNIAL STREAM
MUNICIPAL BORROW PIT
SPRAY AREA 3
SPRAY AREA 2
SPRAY AREA 1
PUMP HOUSE
LEACHATE
LAGOON
ABANDONED LEACHING TRENCH
MCS SHED
CULVERT
WELL
LEACHATE COLLECTION TRENCH
COVERED LANDFILL
TREE STUMP PILE
CONTAINER LOADING ZONE
SEWAGE
LAGOON
FENCE
BURN AREA
MORTIMER'S POINT RD
NORTH BAY
N

Figure 1. The Muskoka Lakes sanitary landfill site.

effective, environmentally-sound, and long-term solution to the Muskoka Lakes sanitary landfill seepage problem. At the time of writing, the project was only at the midway point of its 12-month duration. This manuscript, therefore, constitutes a progress report only and will deal more with the study approach taken rather than definitive results and conclusions.

Literature Review

Spray irrigation systems are designed to recycle landfill leachate back into the soil-vegetation ecosystem in such a way that the maximum degree of renovation and attenuation of contaminants is effected before the leachate re-enters the hydrologic cycle as deep drainage within the land disposal area. Through the processes of soil infiltration and interflow in the unsaturated zone, the leachate will be physically dispersed and diluted to varying degrees. Furthermore, inorganic compounds will be chemically precipitated or adsorbed on soil colloid exchange sites and the organic contaminants will be decomposed by the soil microbial population. Both of these chemical processes will contribute both macro- and micro-nutrients and other elements available for plant uptake and concentration in biomass. An additional design criterion is that, before the leachate reaches the groundwater table and flow systems, evapotranspiration be maximized and overland leachate flow (surface runoff) be strictly controlled or avoided. Thus, both biological and physico-chemical forms of treatment are required to encompass the broad range of leachate constituents. This is particularly true of medium aged, inactive landfills like the Muskoka Lakes site since the dominant renovation process shifts from biological to physico-chemical with time reflecting the temporal variability of leachate compounds and concentrations (Totten, Sims, Hubicki Assoc. Ltd., 1983).

A considerable body of research information exists on spray irrigation of municipal sewage wastewaters in both grass and forest ecosystems (Richenderfer et al., 1975; Sopper, 1975; Harris et al., 1976; Papadopol, 1984). Disposal of landfill leachate using similar techniques is a much more recent practice and is not widespread (Nordstedt, 1975; Menser et al., 1978). Like sewage wastewaters, landfill leachate also contains all essential plant nutrients and would seem to have good potential for recycling through ecological systems. The major obstacle to this usage is the excess concentrations of certain elements that have phytotoxic properties (i.e. iron, manganese) and of heavy metals which accumulate in plant biomass. Indeed, it has been widely observed that the direct contact of leachate with plant foliage is phytotoxic, although the precise physiological cause is not clear (Menser, 1981). It is for this reason that the limited experience gained in spray irrigation of leachate in parts of the United States is not applicable to Ontario conditions. Spraying is routinely carried out in the vegetative dormant months of October to April when direct contact between foliage and leachate can be averted. Leachate spraying is not possible in Ontario during this same period due to the occurrence of air temperatures below 0°C (Gartner Lee Assoc. Ltd., 1984). Thus, some degree of biological and/or physico-chemical pre-treatment of the leachate must be effected to remove the more offending contaminants if this means of treatment is to be successfully adapted to Ontario climatic conditions.

Most research work in this area has focused on comparing the efficiency of various grass species as contaminant concentrating media as well as studying the relative rates of survival with prolonged applications (Menser et al., 1979a). In this respect, forest trees are not as efficient in utilizing leachate constituents as many agricultural crops (Sopper, 1975). In addition, many of these nutrients are redeposited annually as leaf and needle litter, although in less mobile or more benign forms. With regard to mortality, even irrigation with sewage wastewater has been shown to cause a significant decline in the number of tree seedlings and in understory vegetation. Again the exact causes are not evident although the establishment of radically different soil moisture and fertility regimes are no doubt involved. Deciduous tree species and forage grasses have been shown to withstand leachate irrigations of as much as 155 cm over an 8-month period from October to April (Menser et al., 1979b). Observed depression in growth may be related to the low aeration levels in the soil rooting zone induced by high COD leachate application (Menser, 1981).

Methodologies and Preliminary Results

Within the broad objective stated earlier, four more precise areas of investigation provided the terms of reference for the 1986 field season. These were studies of site hydrology and leachate volume reduction, soil quality for leachate disposal, ecosystem stress from leachate irrigation, and physico-chemical pre-treatment of leachate. The ensuing sections provide an inexhaustive outline of the research activities under each heading as well as some preliminary results.

1. Site Hydrology and Leachate Volume Reduction

A major research effort was directed toward identifying means of reducing the total volume of leachate being generated and handled at the Muskoka Lakes site due to the recent expansion of the actual spray area in 1985 and the uncertainty regarding the long-term attenuation capacity of the local glacio-fluvial sands for land disposal.

Of paramount concern was the ability of the existing silty clay to silty clay loam landfill cap to adequately reduce surface infiltration of precipitation. A grid inventory performed of the cap itself indicated that the clay material was both discontinuous and thin (i.e. less than 10 cm) where present. The incomplete sealing of the landfill was in part a consequence of the lack of locally available clay soil for capping material. Saturated hydraulic conductivities (K_{sat}) obtained on intact cores using the constant head method confirmed both the impermeability of the clay material if properly applied to an adequate depth (minimum $K_{sat} = 5.1 \times 10^{-8} cm \cdot s^{-1}$) and its unsuitability for this purpose if mixed with the local sandy soils in thin lifts (maximum $K_{sat} = 5.5 \times 10^{-4}$ $cm \cdot s^{-1}$). Low altitude false-colour infra-red photography confirmed these cap discontinuities through the observation of differential vegetative moisture stress in areas of the grassed landfill with and without the clays of high moisture holding capacity.

A further experiment is ongoing involving possible alternative capping materials. A series of nine 1m x 1m plots were established on the landfill in 1986 to test the ability of various materials or soil treatments situated under a 5 cm layer of turf to reduce or eliminate downward percolation of precipitation once infiltrated. These treatments included the local sand and the existing sic/sicl cap under both compacted and uncompacted conditions, a bentonite slurry with and without sand incorporated, a bentonite-polyvinyl alcohol (PVA) mixture, an industrial polymer-sand mixture, and plastic. By comparing the volume of water applied to each plot when at field capacity to the volume recovered as interflow over the treated soil layer, a simple moisture balance allows for the calculation of the volume lost to deep drainage. Preliminary results indicate that the industrial polymer-sand mixture and the bentonite slurry approach the total exclusion of water that a plastic liner affords while allowing enough deep drainage to promote microbial decomposition of the landfilled refuse (see Table 1). All other treatments fell well short of the optimum degree of impermeability. Of importance is that the industrial polymer is available at no cost making it a much more attractive option than the expensive plastic liners now used at some landfill sites in the United States. A further investigation is now underway to ascertain the long-term weatherability and strength of the polymer-sand mixture in the field, particularly over a winter season.

Table 1. Results of a soil moisture balance for a single irrigation event on the alternative landfill cap plots.

	Soil Moisture Balance for Irrigation Event - Sept. 20, 1986			
Soil Treatment	Depth of Irrigation	- Actual Evapotranspiration	= Runoff Collected	+ Deep Drainage
	mm	mm	mm	mm
Plastic	8.10	2.43	5.67	0
Polymer-sand	8.10	2.43	4.25	1.42
Bentonite slurry	8.10	2.43	4.66	1.01
Bentonite - PVA	8.10	2.43	3.14	2.53
Bentonite - sand	8.10	2.43	2.84	2.83
Existing clay cap	8.10	2.43	1.82	3.85
Compacted clay cap	8.10	2.43	0.81	4.86
Sand (control)	8.10	2.43	2.73	2.94
Compacted sand	8.10	2.43	2.94	2.73

A second research effort in the hydrology area was aimed at reducing the quantity of groundwater in contact with the landfilled refuse. An extensive piezometer network was installed early in the project to determine the major groundwater flow patterns in the vicinity of the landfill. From this it was found that a natural ravine located immediately to the north of the landfill diverts groundwater flow originating from the north toward the perennial stream, thus circumventing any direct contact with the landfill. An exposed bedrock ledge situated upgradient and adjacent to the landfill further diverts any groundwater flow from the east around the landfill. Thus, major groundwater diversion works are not believed to be necessary at this site. Indeed, most of the leachate collected on an annual basis can be accounted for by rainfall amounts directly incident on the landfill area.

In order to test the feasibility of dewatering the area beneath the landfill to eliminate any leachate mounding in the refuse, a 6 m long x 75 cm diameter steel culvert and a number of piezometers were installed at the base of the landfill (see Figure 1). The location for the well was determined with the use of a Geonics EM31 electromagnetic induction meter in an area of apparent concentrated leachate flow. This instrument, by enabling the mapping of concentration isolines, also confirmed the general direction of groundwater flow as being from the landfill to the leachate collection trench. A pump test performed on the culvert well established that the drawdown was significant even after only eight hours of maintaining the well at its minimum level (i.e. 20 cm drop in a piezometer 10 m distant). It is anticipated that continuous pumping from this well would improve the quality of the leachate with time as the groundwater was removed from direct contact with the landfilled refuse.

2. Soil Quality for Leachate Disposal

The present spray area of 4.3 ha is made up of two distinctly different landscape units. Spray areas 1 and 2 (see Figure 1) consist of a shallow veneer (less than 2 m deep) of rapidly permeable fine and medium sands with occasional silty or gravelly substrata. Spray area 3 is comprised of deeper and more homogeneous fine and medium sands (generally greater than 3 m deep) with few textural discontinuities. The recommended design application rates of $2.3 \times 10^4\ \ell\cdot ha^{-1}\cdot day^{-1}$ (April, May, September, October) and $3.4 \times 10^4\ \ell\cdot ha^{-1}\cdot day^{-1}$ (June-August) have been based on a very simplistic water balance with little regard for soil infiltration rates, water storage capacities, attenuation capacities, depth of bedrock, or the composition of the leachate itself. This segment of the study involved the characterization of the local soils and their water regimes both in situ and in the laboratory in order to refine these application rate recommendations.

Table 2 outlines the extent of volatile organic loss from the point that the leachate leaves the vicinity of the landfill in the groundwater flow system (i.e. culvert well sample) to the point when it is ejected from the spray nozzle. Loss of metallic inorganics from the leachate collection trench to the settling lagoons is not as marked, with iron (Fe) decreasing from 49 to 11 $mg \cdot \ell^{-1}$.

Of equal importance to contaminant concentration changes along the collection-disposal system is the distribution of spray around the nozzles and with distance from the pumping station. The overhead spray nozzle type used in this system results by design in an exponential decline in irrigation water depth with distance from the nozzle. This, when combined with the appreciable line pressure drop with distance from the pumping station as well as the frequent malfunctioning of individual nozzles and pump breakdowns in 1986, gave rise to a serious leachate distribution problem over the three spray areas.

Table 2. Loss of volatile organic contaminants along the Muskoka Lakes leachate collection - disposal system.

Volatile* Organic Species	Sampling Location (July 31, 1986)			
	Culvert Well	Leachate Collection Trench	Leachate Settling Lagoons	Spray Nozzle
	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$
Toluene	1900	2000	106	138
Meta-xylene	100	42	0	6
Ortho-xylene	62	25	8	6
Ethylbenzene	54	23	0	0
Trichloroethylene	18	0	0	0
Benzene	17	8	0	0

* volatile organic analyses performed at the Ontario Ministry of the Environment laboratories.

Soil characterization in the field included a number of detailed soil pit descriptions which revealed the presence of fully developed or developing iron-indurated B horizons ("ortsteins"). Most soils examined belong the Sombric or Dystric Brunisol Great Groups and are in the embryonic stages of the "podzolization" soil-forming process. Large loadings of iron-laden leachate thus accelerate this process leading to major soil morphological changes which can radically alter a soils water and fertility regimes.

The fate of leachate contaminants in the soil was ascertained at three "monitoring stations" with the use of suction lysimeters installed from 15 to 120 cm below the surface. In addition, the soil water regimes of these stations were characterized using a network of tensiometers installed also from 15 to 120 cm below the surface, a neutron thermalization soil moisture depth gauge, and groundwater table observation wells. Field saturated hydraulic conductivity (K_{fs}) was further measured using the Guelph Permeameter method. A mean K_{fs} of 7.5×10^{-3} $cm \cdot s^{-1}$ was obtained in the deep, unirrigated sands near spray area 3 which corresponds to the high conductivity (H1) category of the Agriculture Canada macrostructural description scheme (McKeague et al., 1986). A methylene blue dye infiltration experiment on the forest floor indicated that significant quantities of surface applied leachate can move rapidly to depths beyond the root zone by preferential flow along old root channels. The importance of the forest litter layer in leachate retention and renovation is exemplified by the measured $\phi(\theta)$ soil moisture characteristics for a sandy soil outside of the spray areas (see Figure 2). The LFH/Ah horizon will be in a constant state of flux with irrigation between a near saturated state and the permanent wilting point (θv = 86-39% $m^3 \cdot m^{-3}$) whereas the C horizon will remain closer to a metastable equilibrium between 29% and 9% $m^3 \cdot m^{-3}$.

Soil attenuation capacities are further being evaluated in a leaching column experiment. Intact soil columns (4.5 cm diameter x 75 cm long) were extracted in clear acrylic tubes from both sprayed and unsprayed locations. These columns are being subjected to surface applications of raw leachate as well as lime- and activated carbon-treated leachate at rates of 3, 7 and 14 $mm \cdot day^{-1}$. Soil morphological and chemical changes are being monitored for each treatment as is the quality of the liquid extracted periodically at the base of the columns. The use of sprayed and unsprayed soils will also assist in determining the effect of leachate spraying on long-term soil attenuation capacities.

3. Ecosystem Stress from Leachate Irrigation

The visible damage observed in 1986 and previously in the tree and understory vegetation within the spray areas indicates that the practice of spray irrigating leachate into the hardwood forest ecosystem is effecting major stresses on the biota. At this point in the study, the key stresses are thought to be related to i) the phytotoxicity of leachate in direct contact with plant foliage and roots and, ii) marked changes in the soil moisture and aeration regimes brought about by excessive and inequitable application rates of relatively high COD wastewater (i.e. about 1200 mg $COD \cdot \ell^{-1}$).

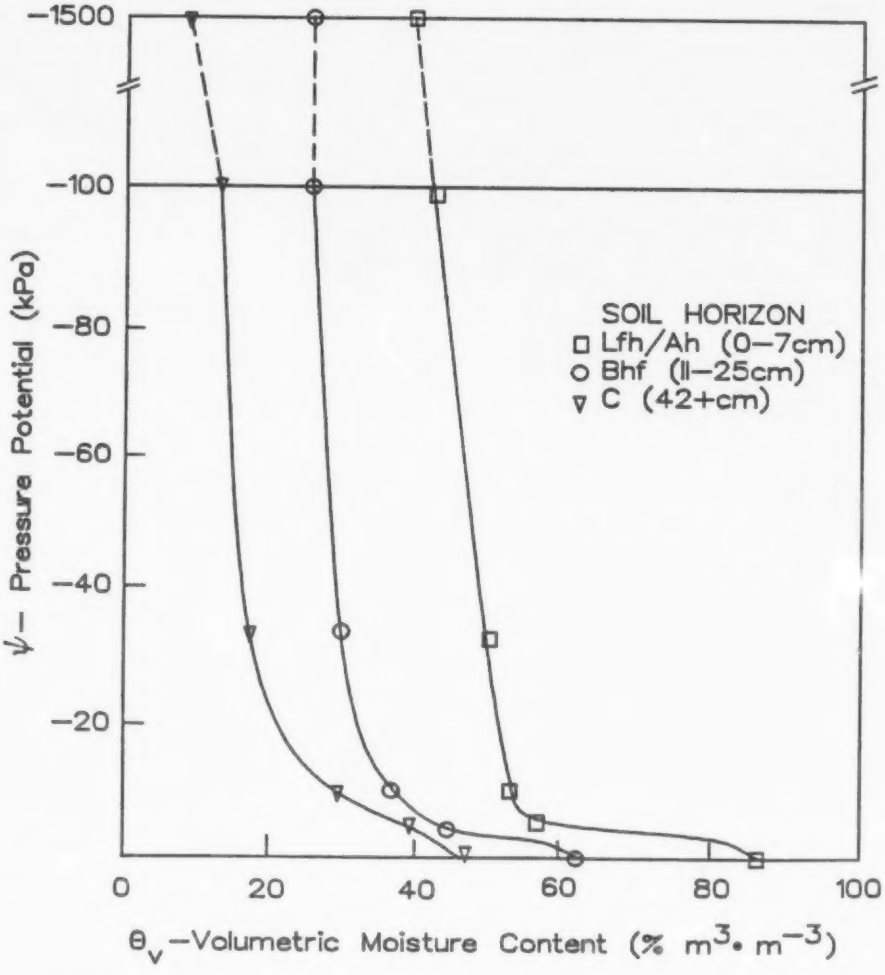

Figure 2. Measured ψ(θ) soil moisture characteristics for three soil horizons from an unsprayed soil.

Vegetative and soil microbial stresses were measured in the field using a number of techniques. Time sequenced, low altitude infra-red photographs demonstrated that vegetation decline and mortality is likely a threshold phenomenon. Spray areas 2 (moderate spray rate) and 3 (light spray rate) showed little visible evidence of stress on the photography while tree canopies in spray area 1, which received a heavy spray loading in the spring of 1986, showed lighter shades of magenta compared to unsprayed trees (Murtha, 1972). Several large gaps in the canopy were clearly visible to the southwest of the leachate lagoons where a more limited spray program was undertaken in the early 1980's.

A total of nine circular, 0.1 ha plots were established in 1986, three in each of a control area (north of the hydro corridor), light spray area 3 and heavy spray area 1 (see Figure 1). Tree growth and productivity measurements in the plots included mid-canopy foliage samples for plant nitrogen determination and stem increment borings for assessment of age and annular ring width using the T.R.I.M. system.

The influence of leachate spraying on forest transpiration and leaf stomatal resistance was measured in the understory and tree mid-canopy with a Li-cor LI-1600 steady state porometer. Some of the results for beech and maple understory vegetation are given in Table 3. Porometer measurements taken on the same day under relatively constant atmospheric conditions for the beech understory show a significant increase in diffusive resistance and decline in transpiration rate with increasing intensity of leachate spraying. A similar trend is evident for maple seedlings even under variable ambient environmental conditions on different sampling dates. This information was complemented by a study of understory community dynamics which sought to relate the presence of certain hydrophilic species (e.g. sedges - Carex spp.) to the transition to wetter soil moisture regimes in the spray areas.

The importance of soil microbial populations to plant nutrient availability and uptake (e.g. mycorrhiza) and to the renovation of leachate in a forest ecosystem prompted a further study of spray irrigation-induced effects on soil microbes. Figure 3 provides the results from a microbial biomass experiment performed in August and October, 1986 on soil cores taken at three depths and in two different spray environments plus a control. The biocidal procedure involves the measurement of the difference in total organic carbon between chloroform-fumigated and non-fumigated soil cores which represents an approximate measure of soil microbial biomass (Jenkinson

Table 3. Measurements of diffusive resistance and transpiration rates of beech and maple understory vegetation exposed to leachate spraying.

Understory Species (sampling date)	Treatment	Sample Size (n)	Means (Standard Errors in Brackets)				
			Diffusive Resistance	Transpiration Rate	Photosynthetically-Active Radiation	Relative Humidity	Leaf Temperature
			$s \cdot cm^{-1}$	$\mu g H_2O \cdot cm^{-2} \cdot s^{-1}$	$\mu E \cdot m^{-2} \cdot s^{-1}$	%	°C
Beech							
(Aug.31/86)	Control (non-spray)	29	2.78 (0.075)	4.127 (0.091)	13.5 (1.25)	34.69 (0.037)	21.0 (0.05)
(Aug.31/86)	Moderate Spray	34	3.47 (0.110)	3.422 (0.107)	176.9 (55.47)	34.77 (0.047)	21.3 (0.11)
(Aug.31/86)	Heavy Spray	29	3.69 (0.140)	3.207 (0.117)	21.2 (4.56)	34.54 (0.019)	21.0 (0.02)
Maple							
(Aug.13/86)	Control (non-spray)	95	3.21 (0.094)	3.776 (0.106)	29.9 (4.99)	38.47 (0.50)	22.0 (0.06)
(Aug.18/86)	Moderate Spray	117	5.20 (0.209)	1.557 (0.067)	54.9 (15.74)	63.79 (1.02)	22.6 (0.16)
(Aug.11/86)	Heavy Spray	83	6.94 (0.290)	1.564 (0.069)	219.6 (37.92)	42.01 (0.01)	19.3 (0.05)

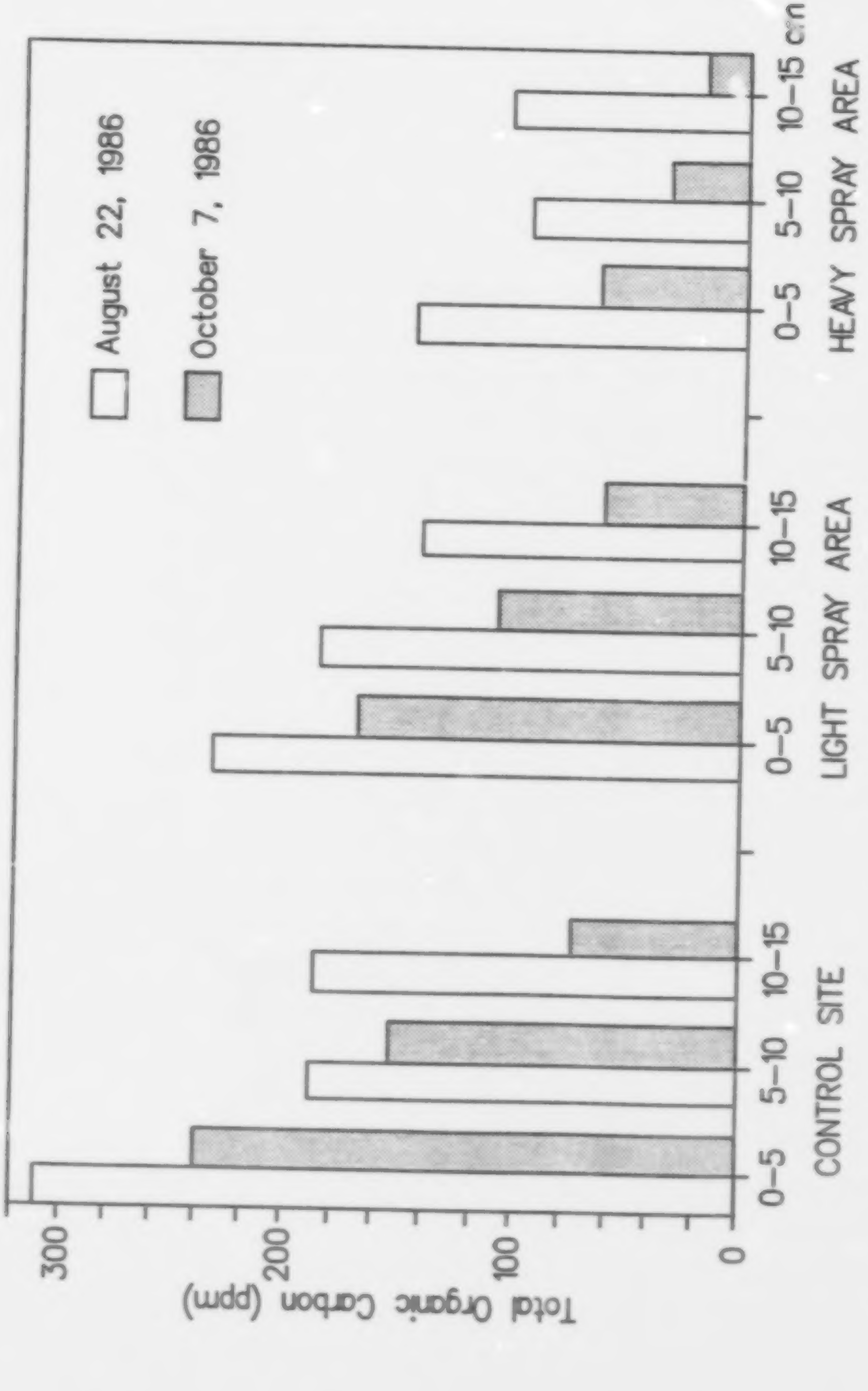

Figure 3. Total organic carbon from soil microbial biomass after biocidal treatment with chloroform.

and Powlson, 1976). Apart from the expected decline in microbial biomass between summer and fall and with depth in the soil, Figure 3 shows a significant decrease in biomass with increasing intensity of spray irrigation at comparable soil depths. A concurrent microbial respiration experiment conducted on the same nine permanent plots, however, did not support the supposition that microbial activity would follow the same trend. A shift in microbial species with wastewater irrigation is presently being investigated as a possible explanation of this inconsistency.

Vegetative and soil microbial stresses are also being investigated in an atmospherically-controlled greenhouse environment. Potted red and sugar maple seedlings have been subjected to a prolonged series of treated and untreated leachate applications to the soil and/or the plant leaves in order to study possible plant physiological changes and partitioning of assimilated contaminants amongst the plant roots, stems, and leaves. Apart from some foliar staining, very few visible symptoms have been observed when leachate is applied at rates sufficient only to meet the atmospheric evapotranspirational demand. Other related ongoing experiments include sugar maple seedling response to soil waterlogging with leachate and soil nitrogen mineralization rate changes with wastewater irrigation.

4. Physico-chemical Pre-treatment of Leachate

A final area of investigation in this study is the determination of an appropriate physico-chemical means of leachate pre-treatment to minimize the adverse effects of spray irrigation on vegetation and soils at the Muskoka Lakes site. A necessary precursor to this study phase is the resolution of the nature of observed phytotoxic effects on vegetation and the scope of soil physical and chemical property changes with prolonged irrigation. Priority pollutant analyses indicate that toluene and Fe are the organic and inorganic constituents of highest concentration, respectively. Both organic and inorganic contaminants can be removed to differing degrees using techniques as varied as high pressure reverse osmosis, upflow sludge bed-filters, downflow stationary fixed-film reactors, activated carbon filtration, aeration, slaked lime addition, and filtration through natural materials such as peat moss or tree bark. Some of these methods can be used together in multi-phase treatment, such as the Environment Canada mobile RO/activated C unit. Lime pre-treatment of leachate to remove metals, however, has proven incompatible with upflow sludge bed-filtration systems which lower effluent COD (Kennedy and Guiot, 1986).

A laboratory pre-treatment study is being conducted which will compare the relative effectiveness of activated carbon (Calgon Filtrasorb 300), $Ca(OH)_2$ (0.25-2.50 mg•ℓ^{-1}), aeration, and filtration through bark of various tree species in removal of Fe and toluene from leachate samples. Aeration or addition of slaked lime causes the rapid precipitation of ferrous iron and promotes volatilization of many organic compounds. While there are no cation exchange sites in activated carbon for the adsorption of Fe, it has been observed thusfar in this experiment that Fe readily precipitates on the granular carbon surfaces. This, when combined with the broad spectrum removal of organic compounds by the activated carbon, effects a high degree of leachate renovation. Tree bark has been successfully used to remove Fe, Al and Mn from drainage wastewaters through the formation of organic complexes ("chelates") with tannins and phenolic compounds (Vaughan et al. 1984). For example, 1 tonne of dry, weathered pine bark can irreversibly absorb at least 65 kg of elemental Fe from wastewater. Under the present conditions at Muskoka Lakes, this quality of bark would become saturated with Fe after about 18 days assuming a 50 ℓ•min^{-1} mean flow rate and 50 mg•ℓ^{-1} Fe in the leachate.

Summary

Investigations made of site hydrology suggest that large scale groundwater diversion works are not required at the Muskoka Lakes landfill. The long-term resolution of the leachate generation problem, however, rests on the achievement of both a suitable reduction in landfill cap infiltration and removal of groundwater in contact with the landfilled refuse through site dewatering. With prolonged pumping, the leachate quality should improve with time.

Given the nature of the local soils, the forest floor litter layer is key to increasing the residence time of the wastewater in the unsaturated zone and effecting a suitable level of renovation before the effluent reaches the groundwater table. High water table levels and shallow bedrock over much of spray areas 1 and 2 greatly reduce this residence time and cause the formation of leachate breakouts in depressional areas. The wastewater distribution system is currently less than satisfactory which gives rise to localized application rates far in excess of evapotranspirational demand and soil attenuation capacity. The removal of Fe from the leachate is necessary to avert major soil morphological changes with long-term spray irrigation.

Major transformations in the soil water regime due to heavy leachate loadings and soil morphological changes are responsible for adverse impacts on forest microbial populations, forest understory communities and tree vigour. More specifically, spray irrigation of leachate induces a relatively rapid forest decline caused by a sequence of factors as outlined in Table 4.

With total treatment of leachate (reverse osmosis/activated carbon), it may be possible to discharge the permeate into the perennial stream without the need to spray irrigate. With partial treatment to remove Fe only (tree bark, lime, aeration), spray irrigation could be continued with more aesthetically acceptable results and with less forest decline if a better distribution system were implemented. A combination of total (winter) and partial (summer) treatment would reduce treatment costs and lead to an environmentally acceptable resolution of the leachate disposal problem at Muskoka Lakes.

Table 4. Factors responsible for forest decline at the Muskoka Lakes landfill site.

Predisposing Factors	Inciting Factors	Contributing Factors
- coarse soils shallow to bedrock (deficient water and nutrient availability, inadequate root support)	- micronutrient (Fe, Mn) imbalance - low soil oxygen caused by waterlogging and high COD leachate - formation of indurated Fe horizon of low permeability in soil - reduced photosynthesis and transpiration caused by excess soil water and foliar staining in understory	- insect, disease and microbial infestations (e.g. bark beetle, needle fungi viruses, root-decay fungi)

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CODISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES. PART II

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Key words: Industrial Solid Waste, Municipal Waste Landfill, Codisposal, Leachate.

This work is part of a longer term study of factors involved in the mobilization of metal species from solids contained in a landfill environment. Current methods of testing for the suitability of solids for disposal in municipal landfill sites do not take into account the anaerobic environment generated by microbial action or the role of biological metal mobilization, and thus the screening tests may not provide the appropriate information required.

In an earlier report the standard EP leach test for a steel flue gas dust was compared with modified leach tests with mixed municipal refuse and the steel flue gas dust. In this report , results from experimental landfill test columns are presented. The columns are designed to provide data on metal mobilization within a municipal refuse landfill with and without various loadings of the steel flue gas dust. Both atmospheric and controlled water input are compared.

The results of the work show that the presence of the industrial waste has a beneficial effect in inhibiting the release of many metal species over the timeframe studied.

Introduction

The disposal of solid wastes has traditionally been carried out by landfill methods because of public acceptance and economics. Despite the long history of this technique, little is known of the complex interactions that take place within a landfill site. Thus the classification of solid wastes into those suitable for disposal with municipal solid wastes and those considered hazardous and therefore requiring disposal with industrial wastes in secure landfill sites, is not based on the behaviour of the waste in the landfill environment, but rather on laboratory screening tests. With growing public concern over all types of disposal sites, it is important to review the screening tests and to correlate the data with observed behaviour. It is in this context that the present work is given.

The study currently in progress has a much broader scope to investigate and model the factors involved in metal mobilization within the environment of a municipal solid waste landfill. This investigation will permit the rationalization of criteria for solid waste disposal and ultimately allow better landfill practices.

The most widely accepted screening tests for determining the suitability of solids for disposal with municipal refuse are the U.S. Environmental Protection Agency's EP test, and the Ontario Ministry of the Environment's LEP test. Both utilize a 24 hour leaching period with acetic acid added as a buffering agent. The conditions of liquid to solid ratio, temperature, amount of acid, and type and rate of tumbling action are set so that reproducible measurements can be obtained. As a result of the time frame of the test, it is unlikely that conditions representing a landfill environment are properly considered. In particular, the factors that clearly are not included are:

- the anaerobic nature of the landfill
- the metal complexation by microbial action and organic species
- the attenuation processes occuring in the municipal refuse
- the effect of the waste on the microbial population of the municipal refuse environment
- the pH buffering capacity of the leachate generated within the landfill

It should be pointed out, however, that the significance of these various factors has not been established, so that the limitations of the screening tests cannot be accurately gauged. In order to evaluate these factors, a two part experimental program was begun.

In the first part, the leaching behaviour of a steel flue gas dust was studied using the LEP method and several variations. This work was reported previously (1). In the second part, leaching columns (193 cm x 33 cm diameter) were set up for measurements of leachate quality of municipal waste with and without industrial waste (the flue gas dust). Thus a comparison of the leach test results can be made with the simulated landfill measurements. The column measurements representing the simulated landfill conditions were run with both atmospheric conditions and intermittent controlled water additions. Four compositions were tested: municipal solid waste (MSW), municipal solid waste with 8% industrial waste (by weight) (MSW + 8% IW), municipal solid waste with 30% industrial waste (MSW + 30% IW), and 8% industrial waste in sand (8% IW + sand). The industrial waste used was from the same batch of steel flue gas dust and was layered rather than dispersed in the municipal waste.

Methodology

Short Term Laboratory Leach Tests

1. LEP Tests

The extraction procedure used in this work followed the LEP method with the proportions reduced to treat 50g of solid rather than the 100g usually employed. In brief, the technique consists of adding 50g (dry weight) of solid to a 1250mL polyethylene bottle with 800mL of deionized water. The pH is adjusted with acetic acid to pH 5.0, provided that the addition not exceed 4 mL of 0.5M acetic acid per gram of sample. The polyethylene bottle is placed on a rotary extractor for a 24 hr period. The solution is then made up to the 1000mL amount to give a 20:1 liquid to solid ratio. The resulting solution is analyzed using standard procedures. The details of the procedure may be obtained from the Ontario Ministry of the Environment.

2. One Month Leach Tests

Solid samples of 50g consisting of municipal solid waste (MSW) and MSW + 8% industrial waste (IW) were treated with the same 20:1 solution to solid ratio using the acetic acid solution described above and deionized water. In these tests, polyethylene bags were used and were hand agitated on a daily basis. Analyses were conducted in an identical manner to the LEP tests.

Long Term Column Tests

A schematic of the columns used is shown in Figure 1. The details have been previously described (1). Four different column compositions were tested: MSW, MSW + 8% IW, MSW + 30% IW and 8% IW + sand. One column for each composition was left open to the atmosphere to receive natural precipitation, and one column for each composition was closed to receive regular water additions, according to an 11 year average monthly rainfall. Each of these columns was run in duplicate giving a total of 16 columns. The columns were insulated and heated in the winter period to avoid freezing. The leachate which collected at the base of the columns was pumped out on a weekly basis to simulate the unsaturated flow found in landfill sites, and samples were taken and analyzed.

Analysis

Samples were analyzed by both ICP (inductively coupled plasma) spectroscopy, and NAA (neutron activation analysis). A total of

18 elements could be analyzed by ICP, though only 12 were measured on a routine basis: Mg, Al, Mn, Cu, Ca, Fe, S, Pb, Zn, Cd, Ni, and Cr. NAA was used routinely for 9 elements: Mg, Al, Mn, Cu, Ca, Br, Na, K, and Cl. The element overlap for the two analytical techniques allowed for cross checking. In addition, NBS standards were used to calibrate the methods. In general, excellent agreement was found for the two methods.

Municipal Solid Waste

The municipal solid waste (MSW) used in this study was collected in the Metropolitan Toronto area. A blend of summer and fall samples was used. The compositon, shown in Table 1, was provided by the Ontario Centre for Resource Recovery. The MSW was shredded for uniformity, and a screen size analysis is shown in Table 2. The metal content of the MSW by ICP and NAA is shown in Table 3.

Industrial Waste

The industrial waste used in this study was collected from a steel producer in Ontario. A chemical analysis of the IW is shown in Table 4. A particle size distribution of the IW is shown in Table 5.

Results

Short Term Tests

The LEP test results for MSW, MSW + 8% IW and IW are shown in Table 6. It is clear from the results that the industrial waste would not pass the screening test, based on the amount of lead solubilized. This is a consequence of the alkaline nature of the IW and the limit set for acid addition in the test. The steel flue gas dust has sufficient sodium, potassium and calcium oxides (or hydroxides) to maintain an alkaline condition after 0.1 moles of acetic acid have been added. The consequence is that the solubilities of certain metals (Mg, Al, Mn, Cu, Fe, Zn, and Cd) are suppressed. This is especially obvious from the fact that all these elements are more concentrated from the 8% IW sample. The elevated concentration of lead is due to the biplumbite ion which is soluble in alkaline conditions.

The leach test using MSW + 8% IW shows values that appear to be more realistic, that is, the presence of the IW has increased the concentration of most species. In this test, the maximum levels for lead (5.0 ppm), cadmium (0.5 ppm) and manganese (5.0 ppm) are exceeded, though only by minor amounts (3.7 ppm, 0.23 ppm and 8.3 ppm respectively). The results of the MSW + 8% IW test conducted for a one month period using the static bag technique also are shown in Table 6. In this case there was sufficient time to develop biological action. This has resulted in an enhancement of some metal concentrations such as Mn and Fe, and now has elevated these above desired levels.

Thus from the standard LEP test, the IW would be considered to pose a hazard, but this is the result of the very alkaline nature of the industrial waste. The combination of IW with MSW in the 24 hr LEP test shows that the alkalinity will be reduced, and that lead levels would be close to the maximum target values. However, comparison of the 24 hr LEP test for MSW and MSW + 8% IW shows that the presence of IW increases the concentration of all elements measured, with Cd, Mn, and Pb now exceeding target values. The one month test, allowing microbial action to take place, shows additional solubilization of Mn and Fe above target values.

Column Studies

A plot of leachate generation for the columns packed with MSW, shown in Figure 2, is typical of the variability found for the leachate production. Despite the greater than average precipitation input to the columns, the leachate volume generation is very similar to the controlled moisture columns, thus showing the effect of evaporation on the atmospheric columns. One approach to providing a common basis for comparison of leachate concentrations is to plot the column data as a function of cumulative leachate volume. This method is attractive for this work because the loss of metal ions from the packed columns is likely to be directly related to the flow of water through the column. Until field capacity is reached for a column, the volume of leachate generated is sporadic, so that column data is shown starting at field capacity. The amount of dry MSW averaged 42.6 kg per column.

A plot of the pH of the leachate as a function of time is shown in Figure 3. As can be seen in the figure, the sand columns have maintained very alkaline leachates over the 300 days past the attainment of field capacity. Three of the MSW columns have leachates with pH values about 5.5, while the fourth MSW column has a leachate with a pH value of about 7.0. The MSW + 8% IW and the MSW + 30% IW columns have leachates which fall between these levels. Thus the presence ofIW in the MSW columns does not appear to modify unduly the pH of the generated leachate. Although the elevation of the leachate pH has been reported, the values in this work appear to be within the range of normal variability. A longer time frame may be required to establish the effect of this IW on leachate pH.

The concentrations of most elements in the leachates were found to decrease with cumulative volume increase. In order to provide a comparison of the effect of codisposed industrial waste, the concentrations of metal ions in the first 30L of leachate were compared. This volume represents about 120 days past the attainment of field capacity and is the period of maximum metal ion concentration. The average and maximum concentrations for 14 elements are shown in Table 7, for the MSW, MSW + 8% IW, MSW + 30% IW and 8% IW + sand columns. It is interesting to note that the maximum concentrations recorded for any of the 4 columns in each set ranged from 2 to 5 times the average value for most elements. The comparison between the column sets show that the presence of IW in the MSW does not increase the amount of metal ion in the leachate with a few exceptions. This is most readily seen by calculating the ratio of element concentration in the leachate to the element concentration found in the MSW leachate. These values are shown in Table 8.

Thus, from the column studies, it appears that there is a synergistic effect between the MSW and IW, which improves the leachate quality for most elements. The problem of high lead contamination predicted by the leach tests does not appear, except for the unbuffered sand columns. Lead levels were somewhat elevated for the column tests, from 1.5 to 4.6 times that of the MSW. The previous indications from the one month test, that iron, manganese and cadmium would be elevated by the presence of MSW and microbial action, was not borne out in the column measurements over the time frame studied. Indeed, the concentrations of these elements were suppressed in the MSW + 8% IW leachate. It is not known whether the beneficial action of the IW in the MSW is a long term effect, or whether once the alkalinity has been neutralized, the concentrations will begin to increase.

Conclusions

The screening tests used for determining the suitability of solid wastes for disposal with municipal waste do not appear to adequately account for the buffering capacity of the MSW environment.

Short term (24 hr, 1 month) tests over-predicted the leachability of the IW, or under-predicted the capacity of the MSW for binding contaminants. There was, in fact, an overall improvement of leachate quality with industrial waste codisposed. This effect may be linked to the alkaline nature of the IW, but longer term studies will be required to test whether this effect will persist. A control strategy for limiting the initially high levels of contaminants in landfill leachates , which is suggested by the results, is to use a lime layer in the landfill site.

From the results of the tests to date, codisposal of some solid industrial wastes appears to be very attractive.

Acknowledgements

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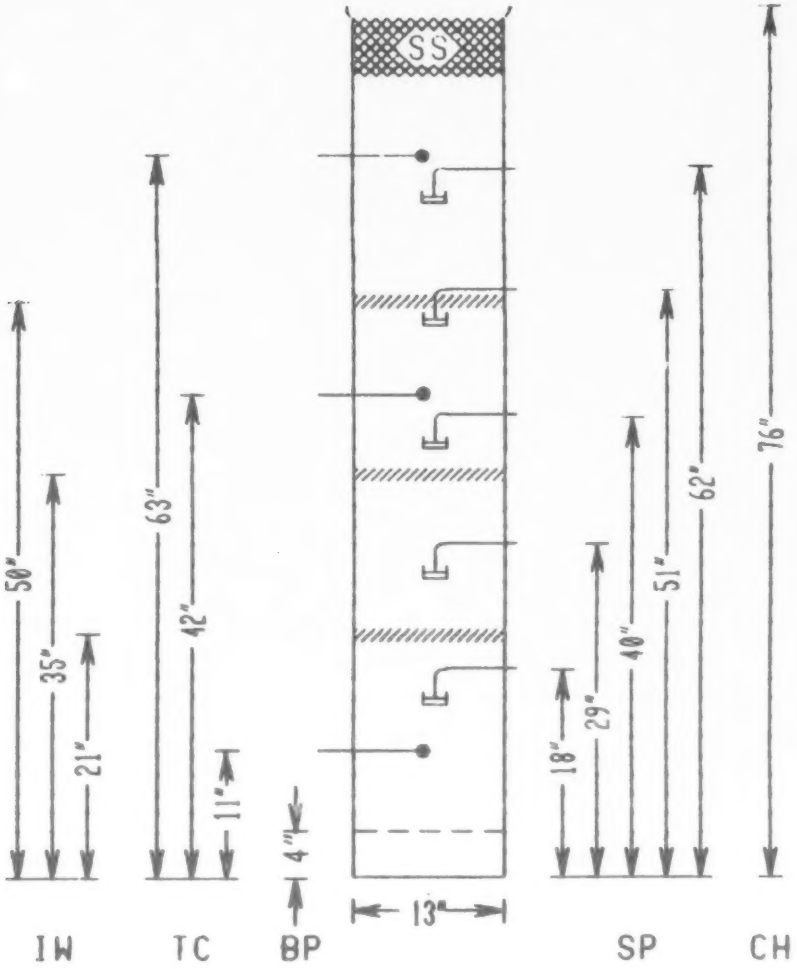
SS
50"
35"
21"
63"
42"
11"
4"
13"
18"
29"
40"
51"
62"
76"
IW
TC
BP
SP
CH

Legend :

IW	Industrial Waste
TC	Thermocouples
BP	Bottom Plate
SP	Sampling Ports
CH	Column Height
SS	Silica Sand

FIGURE 1 Column dimensions and interior

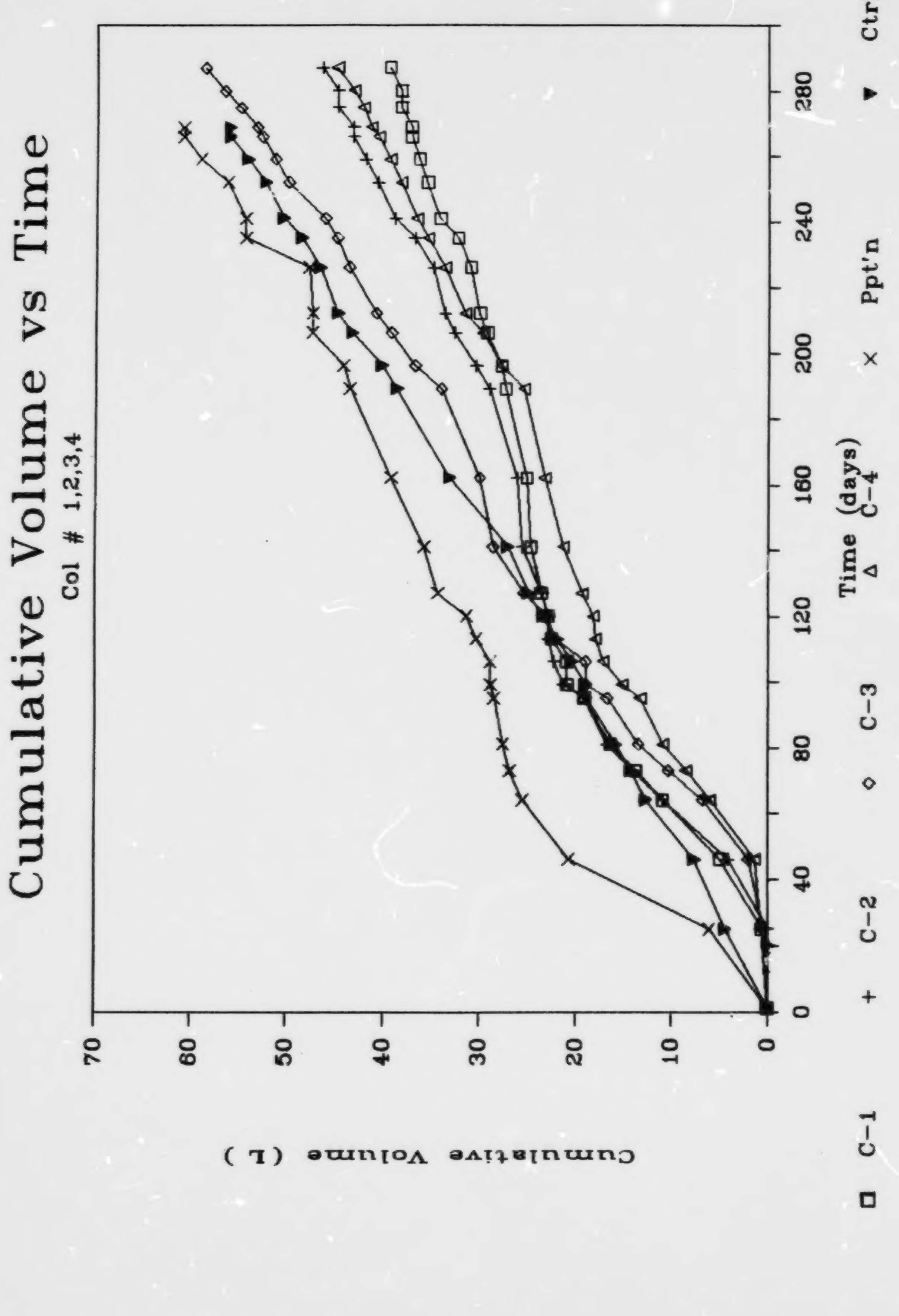
Cumulative Volume vs Time
Col # 1,2,3,4
Cumulative Volume (L)
0
10
20
30
40
50
60
70
Time (days)
0
40
80
120
160
200
240
280
□ C-1
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FIGURE 2

Leachate pH versus Time

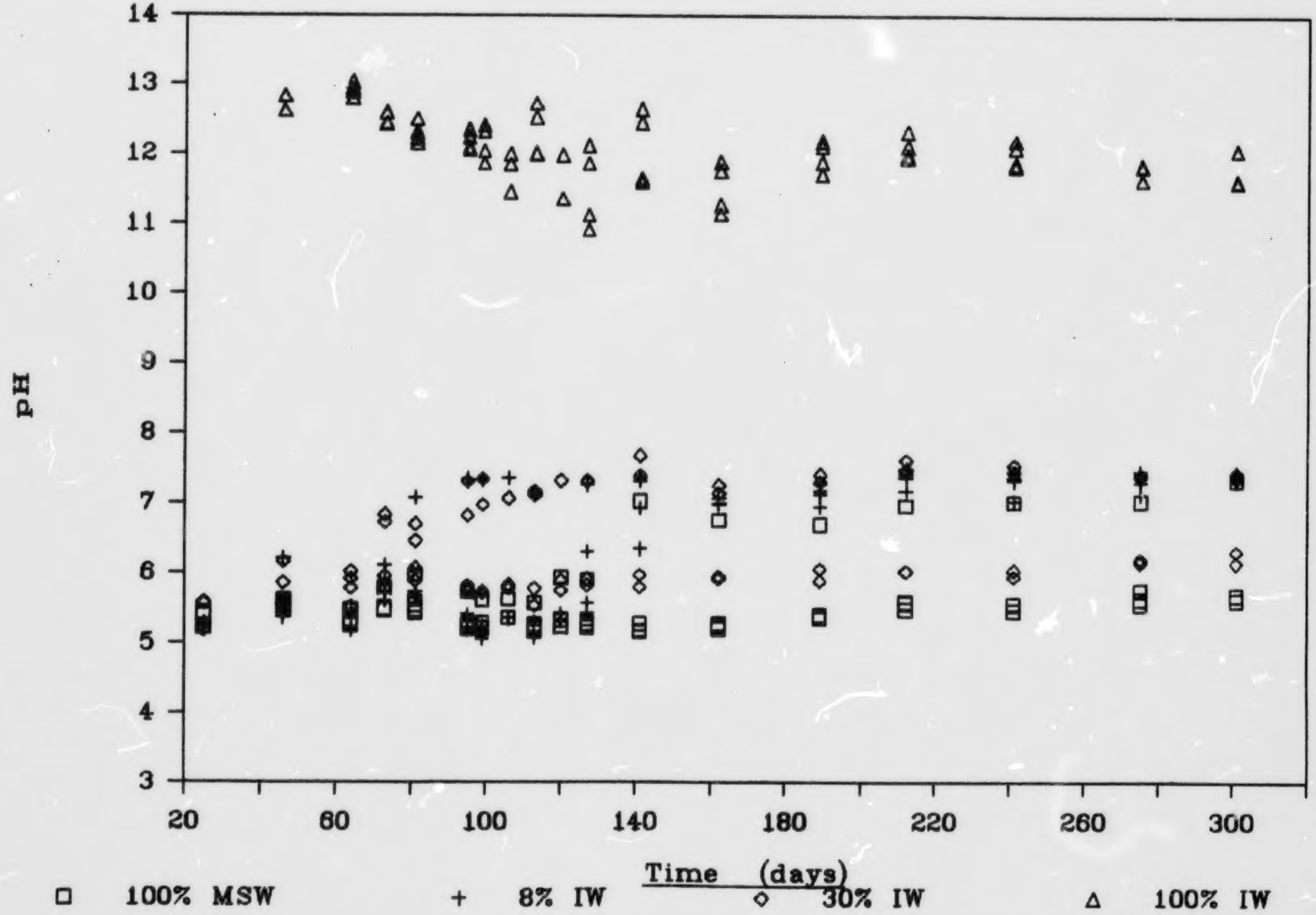

FIGURE 3

TABLE 1

Municipal Solid Waste Composition (by weight)

	Fall Sample (%)	Summer Sample (%)
ash	45 +/- 4	
moisture	27.2	14.0
Component Analysis		
paper	54.0	25.3
natural organic	0.8	17.0
synthetic organic	7.2	20.4
ferrous material	10.1	8.6
nonferrous material	1.5	-
glass	1.2	1.5
fines	24.9	26.5
TOTAL	99.7	99.3

TABLE 2

Size Distribution of MSW After Shredding

Screen Size	% Retained
+4 inch	0.4
+2 inch	4.0
+1 inch	23.8
+1/2 inch	25.6
+1/4 inch	20.4
+8 mesh	14.9
-8 mesh	10.6
TOTAL	99.7

TABLE 3

Metal Content of the MSW by ICP and NAA

Element	Concentration (by weight)
Mg	980 ± 270 ppm
Cu	120 ± 30 ppm
Na	1.06 ± 0.45%
V	8.7 ± 1.6 ppm
Al	1.84 ± 0.04%
Mn	620 ± 20 ppm
Ca	5.1 ± 0.6%
Cr	88 ± 5 ppm
Fe	3.0 ± 0.4 ppm
Zn	680 ± 5 ppm
Co	18 ± 1 ppm
Cl	750 ± 990 ppm
Ni	25 ± 20 ppm
Cd	7.1 ± 0.2 ppm
Pb	90 ± 20 ppm
S	0.64 ± 0.02 ppm
As	40 ± 2ppm
B	142 ± 6 ppm
Ba	270 ± 30ppm

TABLE 4

Metal Content of the IW by ICP and NAA

Element	Concentration (by weight)
Mg	1.51 ± 0.01%
Cu	0.18 ± 0.01%
Na	0.75 ± 0.08%
V	110 ± 10 ppm
Al	0.205 ± 0.004%
Mn	4.0 ± 0.1%
Fe	27.2 ± 0.5%
Zn	14.1 ± 0.3%
Co	16.1 ± 0.8 ppm
Cl	1.34 ± 0.14%
Ni	410 ± 70 ppm
Pb	1.99 ± 0.002%
Cd	323 ± 9 ppm
S	0.36 ± 0.2%
As	90 ± 10 ppm
Mo	46 ± 10 ppm

TABLE 5

Particle Size Distribution of IW

Mesh Screen Size	Cumulative % (by weight)
+80	16.8
+100	20.0
+140	25.5
+200	30.2
+325	36.5
-325	63.5

+ retained - passed through

TABLE 6

LEP Tests (ppm)

	24 Hour Test				1 Month Test
Element	MSW	MSW + 8% IW	IW	Allowable Limits	MSW + 8% IW
Mg	35.3	50	0.44		50.4
Al	1.8	2.3	0.30	<10>	2.01
Mn	3.3	8.3	0.04	<5>	14.4
Cu	0.25	0.63	0.26	<100>	0.40
Ca	390	812	3956	<8000>	373
Fe	3.69	8.32	0.07	<30>	54.1
S	73.8	78.2	85.9		89.0
Pb	-	8.7	175	5.0	9.26
Zn	3.42	254	6.36	<500>	245
Br	0.28	2.40	24.6		2.47
Na	102	112	260	<2000>	128
K	69.5	74.5	232		102
Cl	105	152	720	<25000>	155
Cd	0.05	0.73	-	0.5	0.54
Cr	0.04	0.14	0.45	5.0	0.13
pH	5.8	5.3	11.9		5.2

< > refers to 100X maximum desirable concentration

TABLE 7

COLUMN LEACHATE COMPOSITIONS (ppm)

Element	MSW		MSW + 8%IW		MSW + 30%IW		8%IW + Sand	
	Avg*	Max	Avg*	Max	Avg*	Max	Avg*	Max
Mg	476	858	343	616	358	606	1.04	2.88
Al	6.42	54.3	9.77	30.0	1.65	7.78	2.92	6.22
Mn	50.7	92.9	25.0	60.3	35.2	68.1	0.12	0.03
Cu	0.46	0.89	0.28	0.73	0.48	1.53	0.15	0.37
Ca	2563	4297	1638	3332	1716	3668	363	1922
Fe	813	1095	450	1170	545	1821	0.1	0.52
S	412	690	149	470	411	725	39	258
Pb	0.64	1.40	2.93	22.0	0.94	2.89	109	589
Zn	51.7	113	20.4	54.8	43.5	107	0.69	3.05
Cd	0.48	4.05	0.08	0.18	0.16	0.31	0.02	0.08
Cr	0.39	1.98	0.32	1.55	0.18	0.49	0.25	0.57
As	0.41	0.53	0.16	0.41	0.42	0.57	0.02	0.05
Co	0.29	0.55	0.18	0.50	0.38	1.50	0.03	0.15
Ni	1.45	2.18	0.93	1.90	0.89	2.41	0.06	0.27

* Average of four columns (2 atmospheric + 2 control)

TABLE 8

Leachate Concentration Enhancement versus MSW Leachate

Element	MSW + 8%IW	MSW + 30%IW	8%IW + Sand
	MSW	MSW	MSW
Mg	0.72	0.75	0.002
Al	1.52	0.26	0.46
Mn	0.49	0.69	0.001
Cu	0.60	1.05	0.33
Ca	0.64	0.67	0.14
Fe	0.55	0.67	0.001
S	0.36	1.00	0.1
Pb	4.59	1.47	171
Zn	0.39	0.84	0.013
Cd	0.17	0.33	0.034
Cr	0.80	0.47	0.65
As	0.39	1.04	0.059
Co	0.60	1.28	0.09
Ni	0.64	0.62	0.039

HAZARDOUS ORGANIC CHEMICAL IN GROUNDWATER AT ONTARIO LANDFILLS

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ABSTRACT

Studies have been conducted at seven landfills in Ontario ranging in latitude from the North Bay landfill in the north to a landfill near Sarnia in the south. The sites represent a variety of geologic materials in which migration of leachate-derived contaminants occurs, including sand aquifers, sandy silty glacial till, clayey glacial till and fractured carbonate/shale. With the exception of the clayey till site, extensive lateral migration (> 200 m < 1000 m) of organic contaminants, particularly the common volatile organics, has taken place. These landfills range in age from one to three decades. The total dissolved organic carbon in the contaminated groundwater is generally in the range of 10 to 200 mg/L. The total load of identifiable organic compounds is only a small fraction of this total. The nature of the suite of characteristic volatile organics differs considerably from landfill to landfill, and to some degree reflects the nature of the industrial base of

the municipality. The spatial distribution of volatile organics within each plume is generally more complex than the distribution of the standard plume indicator parameters such as total dissolved solids, electrical conductance, total dissolved organic carbon and chloride. The design of effective monitoring networks for trace organic contaminants is therefore more difficult.

At the landfill on clayey glacial till, the downward migration of Cl^- and volatile organic compounds was determined through work done in collaboration with the Oregon Graduate Center. Vertical cores were collected from the bottom of a five year old hazardous waste-disposal pit in unweathered clayey material. These cores show that downward contaminant migration has occurred due to molecular diffusion without significant influence of groundwater flow. Chloride has diffused 85 cm in 5 years. Volatile organic compounds have moved at a slower rate due to adsorption. The clayey till below the pit site is 26 m thick and therefore the aquifer below is not threatened. In a different context, however, molecular diffusion is a process that will cause contaminants to move through compacted clay liners relatively quickly even if the liners achieve a very low permeability.

INTRODUCTION

It has long been recognized that municipal landfills in Ontario and elsewhere produce leachate that causes contamination of groundwater. Zones of contaminated water, termed leachate plumes, can be quite extensive at landfills situated on permeable geological materials. Since 1976 researchers at the Institute for Groundwater Research have investigated the physical and chemical controls of contaminant migration at such landfill sites. Since 1982 additional emphasis has been placed on the migration of organic contaminants. Some of these organic studies were conducted in collaboration with researchers from the Environmental Engineering Group at Stanford University and from the Department of Environmental Chemistry and Biology at the Oregon Graduate Center.

Seven landfill sites are currently being investigated. Three sites (Borden, Woolwich, North Bay) are situated on unconfined sand aquifers, one site (new Borden) on unconfined sand and clay tills, one site (Tricil near Sarnia) on clayey glacial till, and two sites (Bayview and Hamilton) on fractured sedimentary bedrock. Thus, a wide range of hydrogeological conditions are included in these studies.

Methods of investigation at all but the Tricil site are summarized by Barker et al. (1984). Essentially, an extensive network of multilevel groundwater sampling devices, termed multilevel piezometers, are established to provide a detailed, three-dimensional picture of contaminant distributions. Hydraulic information obtained by water-level measurement, well-testing, and detailed core analysis defines the groundwater flow system responsible for contaminant migration. Hydraulic testing, piezometer sampling , and laboratory studies of sorption and biotransformation can then be integrated, with the assistance of mathematical simulation when appropriate, to describe the migration of organic contaminants in the plumes.

With respect to organic contaminants, these studies are addressing several questions:

1) what organics are present in landfill leachates?
2) how fast do they migrate in groundwater?
3) how far and for how long do they persist? and
4) what are the processes controlling their migration and persistence?

The fourth question is important to address if the results of these field studies are to be generalized for application to other landfill or waste disposal situations. Only a thorough understanding of the processes will establish a reliable predictive capability.

It is important to study real landfill situations where the results of complex, interactive transport processes are fully apparent. This complexity, however, also limits our ability to identify the contribution of specific processes, such as sorption, dispersion, and transformation, to organic contaminant migration and persistence. The major field limitations are the undefined history of inputs from the waste to the groundwater and the uncertainties in the flow system hydraulics. Laboratory studies, under conditions representative of field sites, are often more useful to evaluate specific processes. Another approach currently being emphasized at IGR is to conduct field-scale experiments in which solute-spiked groundwater is injected into a well-characterized aquifer and the migration of solutes under natural flow conditions is monitored by sampling from a dense, three-dimensional network of multilevel piezometers. This provides for a well-defined input and a well-characterized flow system in which the processes can be more clearly investigated. "Natural gradient injection" experiments were used by Sudicky et al. (1983) to study dispersion of chloride, by MacKay et al.

(1983) for selected halogenated organics, by Sutton and Barker (1985) for selected soluble organics, and by Patrick and Barker (1983) for monoaromatic hydrocarbons. Thus, laboratory and field-scale experiments augment the current studies of organic contaminant migration at landfill sites, all with the aim to better understand the processes controlling organic contaminant behaviour in groundwater.

Barker et al. (1985) described some of the current studies at four of the landfill sites, and Barker (in press) expanded the discussion to include six sites. A detailed characterization of landfill leachate was conducted and specific organics were selected for more detailed study. To date, these studies have emphasized commonly encountered, more-mobile organics which can routinely and reliably be determined in numbers sufficient to provide accurate "snapshots" of their distribution in groundwaters. Studies to date have emphasized two classes of volatile organic contaminants:

1) halogenated, one-and-two carbon hydrocarbons which are common industrial chemicals that regularly occur in household products, and
2) aromatic hydrocarbons, occasionally chlorinated, that are common in petroleum products and other industrial chemicals as well as in household products.

Distributions are then interpreted in terms of the hydrogeological processes (advection, dispersion) and geochemical processes (sorption, chemical and microbial reaction) which must control the distributions.

Some results from the 1984 and 1985 field studies at the North Bay landfill will be presented in this paper. Preliminary results from the

Tricil site, located in thick clayey deposits will also be discussed. In the North Bay site, advection is rapid. In the Tricil site, slow diffusion is the dominant process causing transport of organic contaminants.

THE NORTH BAY LANDFILL LEACHATE PLUME

The most intensively studied landfill site is at North Bay, Ontario (Reinhard et al., 1984; Barker et al., 1986). The landfill lies in a complex deposit of bedded glaciofluvial sands underlain by gneissic bedrock. The site has operated since 1962 and leachate-contaminated groundwater has been observed discharging near a creek, about eight hundred meters from the landfill, since our studies began in 1980. Thus, at this site we have not been able to discuss a plume front, as is found at the other sites. Mobile contaminants have reached the discharge zone, albeit at very low concentrations. This study, therefore, cannot deal with relative velocities of contaminants, but rather provides field evidence of contaminant transformation and persistence during transport in anoxic groundwater.

The organic geochemistry of the leachate is presented by Reinhard et al. (1984), Barker (in press), Barker et al., (1985) and Barker et al. (1986). Figure 1 shows the plan view of the leachate plume and the location of piezometers used to construct cross-sections (Figure 2). Tables 1 and 2 presents the geochemistry of groundwaters along the plume for 1983-1984. Figure 2 shows the distribution of the indicator parameter chloride (Cl) and selected aromatic hydrocarbons in the vertical cross-section along the centre of the leachate plume. Volatile halocarbons do not persist throughout this plume, probably due to their biotransformation under the methanogenic conditions of this plume. Volatile aromatics are more persistent, however, and are found occasionally in the discharge zone, although at significant attenuation. Considerable dilution due to dispersion is evident in the declining concentrations of rather unreactive constituents such as Cl, Na, K, Ca and Mg.

Recent hydrogeological studies (M. Moore, 1986 and N. Gensky, M.Sc. thesis in progress) have identified a relatively thick sand of rather uniform appearance and hydraulic conductivity (about 1×10^{-2} cm s^{-1}) probably extending throughout the flow system. Average groundwater velocities appear to be from 4×10^{-4} cm s^{-1} to 1×10^{-3} cm s^{-1}. Unretarded contaminants could, therefore, be moving through the flow system within two to four years.

Spatial and temporal variability of contaminant distributions have been the focus of recent studies (Barker et al., 1985). The general shape of the leachate plume has not changed since about 1980 although there has been considerable fluctuation in the concentration of the indicator parameters chloride (Cl) and dissolved or total organic carbon (DOC of TOC). The general distribution of organic contaminants is similar (Figure 2). Sampling during 1985 on a monthly basis revealed considerable temporal variation in the indicator parameters and aromatic hydrocarbons (Figure 3). This variability may be seasonal, but further data assessment is required to evaluate the seasonality.

There appears to be only a poor correlation between the indicator parameter Cl and the organic contaminant benzene at piezometer G-5 (Figure 3). To evaluate the correlation between indicator and trace organic parameters, a series of simple statistical tests were performed. All the pairs of chloride plus benzene, chlorobenzene, and 1,2,4-trimethylbenzene for groundwaters sampled in 1985 from the multilevel piezometers G, LL and AAA were used. Linear regression equations were developed for the chloride-organic pairs and the linear correlation coefficients calculated. The results are shown in Table 3. Near the landfill at piezometer G, there is essentially no correlation of chloride with the trace organics. This suggests that the leachate input is rather irregular and that the landfill is not a constant source of these contaminants. Further along the flow system at piezometer LL, the contaminants benzene and chlorobenzene show a much better correlation with the indicator parameter. At LL, the 1,2,4-trimethylbenzene concentrations were often below the analytical detection limit (about 0.2 ug/L) and so no correlation was attempted. This improved correlation at lL is intriguing. Could it be that the processes controlling contaminant transport, particularly dispersion, sorption and biodegradation, are acting to smooth the erratic Cl-organic relationship observed near the landfill? This aspect is under investigation (Gensky, M.Sc. thesis, in progress). In the discharge zone the organic concentrations have dropped considerably so that most samples contained only undetectable levels of organics, except for benzene. The Cl-benzene correlation was established by assigning the undetectable benzene concentrations as the detection limit (0.2 ug/L). The resulting correlation is very poor, in part due to this assignment. However, it does appear that the aromatic hydrocarbons are being biodegraded as well. This process probably contributes to the lack of Cl-benzene correlation; biotransformation removes benzene even from high-Cl samples, leaving variable Cl concentrations in samples, with low and less-variable benzene concentrations.

Because of time and financial constraints, leachate plumes are normally monitored infrequently and analysis of indicator parameters is emphasized. Our experience at the North Bay site indicates this is adequate to establish a gross picture of the plume behaviour, but may be inadequate to discuss more subtle, but still significant, changes in contaminant concentrations. The temporal variability of contaminants should be evaluated. Before the concentration of an indicator parameter such as chloride can be used to infer the concentration of another contaminant, a strong correlation of these parameters must be shown throughout the plume. This is certainly not the case in the North Bay plume.

In addition, reactive contaminants are generally unlikely to remain well-correlated to non-reactive indicator parameters during transport. This is particularly true for organic contaminants which are undergoing biodegradation. To illustrate this, consider the decrease in chloride and benzene concentrations as groundwater moves down the flow system from G-5 to AAA-5 (see Tables 1 and 2). Whereas the chloride concentration decreased almost seven-fold, the benzene concentration decreased thirty-two-fold! This difference was typical over the 1984-86 data base. Barker et al. (1986) cautioned that such dramatic organic concentrations declines could not be directly interpreted in terms of the extent of biodegradation due to the considerable temporal variability of both chloride and benzene inputs from the landfill. However, even a caution interpretation of the differences between chloride and benzene decline must invoke biotransformation of benzene. In any case, the inability to predict organic contaminant concentrations from indicator parameter data is obvious.

A LANDFILL ON THICK CLAYEY DEPOSITS

The use of clay liners at waste disposal sites is frequently advocated as a means of minimizing the potential for groundwater contamination. It is commonly thought that if a clay liner has no structural defects and has a low hydraulic conductivity everywhere, the liner will provide a barrier between the waste and the hydrogeologic domain beneath the liner. Guidelines for the properties of clay liners commonly specify that the liner should have a hydraulic conductivity less than 1×10^{-7} cm s^{-1} so that the rate of hydraulic flow through the liner will be small. Advection of contaminants through the liner will therefore be slow. Even when advection is minimal, however, contaminants can migrate through clay liners at rates that may be significant. This non-advective migration is caused by molecular diffusion.

This paper describes an investigation of contaminant migration in a natural clay deposit beneath a completed cell at a hazardous waste-disposal site. The clay is unweathered and has a very low hydraulic conductivity ($< 10^{-8}$ cm s^{-1}). Because of the lack of weathering, uniformity and low hydraulic conductivity, the clay has all of the features normally desired of a clay liner. The purposes of the invectigation are to determine the rates at which inorganic and organic contaminants from the waste migrate downward through the clay and to assess the applicability of simple diffusion models for predicting these rates.

The waste disposal facility, which is operated by Tricil Limited, is located 15 km southwest of Sarnia, Ontario. It is the only landfill in Ontario that receives hazardous wastes exclusively. We selected the site for this study primarily because the natural clay deposit is thick and therefore vertical boreholes through the waste could be drilled a metre or two into the clay without destroying the integrity of the overall deposit. From the bottom of the waste to the bedrock aquifer underlying the clay, the clay is 25 m thick. The site possesses additional attributes, such as waste material that offers no obstructions to drilling, accurate information on the locations and depths of old cells, and hydrogeological conditions that have been determined in detail in previous investigations.

The waste-disposal cell selected for this investigation was excavated in 1979. The cell received its final load of waste in 1980. The waste mass consists mainly of fly ash from a nearby coal-fired electrical generating station. Liquid hazardous wastes were mixed with the fly ash prior to disposal. The cell has a 2 m thick cover of compacted clay.

The study site is situated on a flat clay plain that extends more than 20 km in all directions from the site. The clay deposit which is late Quaternary in age, was formed by glaciers that protruded into a large glacial lake. The deposit contains numerous small pebbles and granules of shale bedrock indicative of the glacial-till origin of the deposit. About 40% of this glacial till is clay-sized particles, which are primarily illite and chlorite (Quigley and Ogunbadejo, 1976). The remainder consists of silt and sand-sized material and a small percent of pebbles.

Desaulniers et al. (1981), and Desaulniers and Cherry (1986) have studied the permeability of the clay, and the flow rates and age of groundwater in the clay at several locations on the clay plain including the Tricil site. The investigators concluded that, below about 5 m from ground surface, the clay is unweathered, has an average hydraulic conductivity less than 5 x 10^{-8} cm s^{-1}, has downward groundwater flow at average linear velocities less than several millimetres per year, and contains water that is very old, generally many thousands of years old. They also concluded that natural solutes in the groundwater, such as Cl^-, Na^+, ^{18}O and ^{2}H have developed vertical concentration profiles dominated by the influence of molecular diffusion during the geologic time. Desaulniers et al. (1986) simulated the vertical concentration profiles by means of one-dimensional diffusion models and diffusion times of 9,000 to 16,000 years.

From analysis of core samples taken from weathered clay at the bottom of a municipal landfill in Sarnia, Goodall and Quigley (1977) and Crooks and Quigley (1984) determined vertical profiles of several inorganic leachate-derived constituents. While the data suggest diffusion as the dominant cause of profile development, they only had limited success in the fitting of a diffusion model to the data. Our investigation has some similarities to the work done by Quigley and co-workers, but our focus is on the clay at greater depth where it is unweathered and on organic compounds rather than inorganic compounds other than chloride.

After sectioning the cores, pore water obtained by squeezing numerous core segments was analysed for chloride and volatile organic compounds. Chloride was detected in the clay to a maximum depth of 90 cm below the bottom of the waste. The most mobile organic compounds were found only to a depth of 25 cm. Although there is a large downward hydraulic gradient in the clay, the downward migration of chloride is caused only by molecular diffusion without significant influence by advection. The smaller distances of penetration for the volatile organic compounds are attributed to adsorption. Because the clay deposit is 20 m thick, it will take thousands of years for contaminants to diffuse through the clay into the underlying aquifer. This study has implications with respect to low-permeability clay liners used at waste disposal sites. The results of this study suggest that for liners of typical thickness (< 1 m), molecular diffusion will cause breakthrough of relatively mobile contaminants in several years or less. The details of this investigation are provided in a paper by Johnson et al. (1986).

CONCLUSIONS

Landfill sites on permeable materials provide a temporally-variable input of contaminants to shallow groundwaters. Groundwater transport processes seem to establish leachate plumes which have far-less variability of extent and shape based on the distribution of indicator parameters. However, it appears that trace organic contaminants still show considerable temporal variability in the groundwater flow system. Also, their concentrations are poorly predicted from the concentration of indicator parameters such as chloride. This is due, in part, to the variability of the input of contaminants from the landfill. Whereas transport processes such as dispersion may act to smooth the input variability, processes such as biodegradation render the relationship between chloride and organic contaminants far less regular.

Molecular diffusion is the dominant transport process at landfill sites on unfractured impermeable clayey deposits. Thus leachate plumes are far more restricted. Organic contaminants appear to migrate even slower than conservative tracers such as Cl, due to sorption. Diffusion-dominated transport is sufficiently slow to provide considerable protection of aquifers at the site on clayey till. However, the protection afforded by thin clay liners is probably far briefer.

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Table 1:

Inorganic Parameters in Groundwater from the North Bay Landfill Leachate Plume. Concentrations are in mg/L Unless Noted Otherwise. Samples Collected 21/11/83

Parameter	Piezometer G-5	LL-5	LL-9	AAA-5
pH	6.9	6.8	6.7	6.4
Conductivity (umho/cm)	4510	1740	2650	560
Ca	232	106	123	50.0
Mg	99	37.5	56	14.4
Na	285	109	197	38
K	230	56.5	81.5	11.0
Alkalinity (as $CaCO_3$)	2070	711	970	220
F	0.06	0.06	0.04	0.04
Cl	332	138	226	50.0
SO_4	15.0	8.0	13	10.0
NO_3 (as N)	<0.1	<0.1	<0.1	<0.1
Kjeldal N (as N)	192	53.5	76.0	12.0
Ammonium (as N)	185	47.5	68.0	7.0
Nitrite (as N)	0.06	0.06	0.08	0.06
DOC	129	46.5	82.0	12.9
Fe	82	90	140	22
Mn	5.6	5.6	8.2	3.4
As (ug/L)	< 1	2	2	1
Ba "	220	1500	2600	270
Cd "	<10	<5	80	<5
Cr "	33	23	38	11
Cu "	<9	<5	<5	<5
Ni "	79	63	100	21
Pb "	67	88	160	<30
Se "	<1	<1	<1	<1
Zn "	6	9	11	8

Table 2: Selected Organic Parameters in Groundwater from the North Bay Landfill Leachate Plume. Concentrations in ug/L Unless Noted Otherwise.

Parameter	**Piezometer**		
	G-5	**LL-9**	**AAA-5**
MOE Lab (20/11/83)			
Lindane (ng/L)	1	<1	<1
Dieldrin "	<1	4	2
DDD "	<5	25	<5
Biphenyl	3	1	n.d.
Polyethylene Glycol Deriv.	180	10	n.d.
Dimethylbenzoic Acid	n.d.	13	n.d.
Tributyl Phosphate	22	15	2
Phthalates	110	50	10
Phenols	10	15	n.d.
Hydroxybenzothiazole	10	<15	3
Chloroform	0.9	-	n.d.
1,2-Dichlorobenzene	13	14	3
Acetone	6	2.4	0.6
Diethyl Ether	15	20	4
Tetrahydrofuran	9	5	0.6
Methyl Ethyl Ketone	2	0.8	n.d.
Thiophene	0.6	n.d.	n.d.
1,4-Dioxane	0.6	n.d.	n.d.
Diethyl Sulphide	3	n.d.	n.d.
Hexanol	11	6	n.d.
Fenchone	48	27	n.d.
Camphor	19	n.d.	n.d.
UW Lab (26/10/84)			
Benzene	51	13	1.6
Toluene	1.3	n.d.	n.d.
Chlorobenzene	9.1	6.9	n.d.
Ethylbenzene	58	13.6	n.d.
p-Xylene	90	-	n.d.
o,-m-Xylene	7.6	-	n.d.
Cumene	6.6	2.8	n.d.
1,2,4-Trimethylbenzene	51	2.7	n.d.
Napthalene	15	n.d.	n.d.

Table 3: Slope (m) and Intercept (c) for the Relationship Between Chloride and Various Organic Concentrations, Where Organic = m x chloride + c. The linear Correlation (Coefficient of Correlation r) Between Chloride and Organics is also shown.

Location	Organic	No. of Data	Slope (m)	Intercept (c)	Linear Correlation (r)
G	Benzene	66	1.30	31.0	-0.0968
	Chlorobenzene	66	2.51	13.8	0.0231
	1,2,4-Trimethylbenzene	66	-0.145	90.6	-0.511
LL	Benzene	72	-0.0643	-0.13	0.773
	Chlorobenzene	72	0.0551	1.78	0.622
AAA	Benzene	21	-1.18	1.61	-0.113

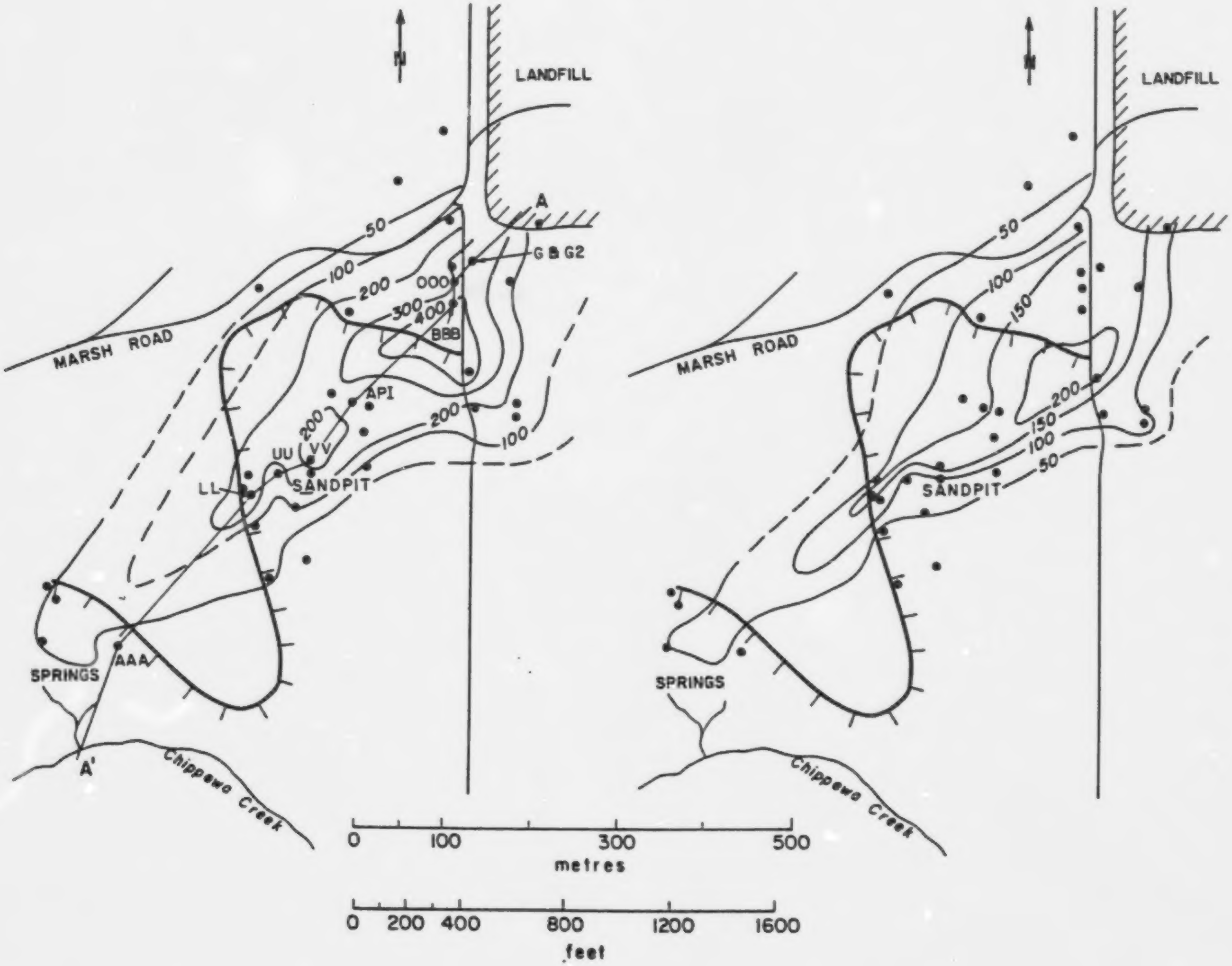
N
LANDFILL
MARSH ROAD
50
100
200
300
400
000
BBB
G & G2
A
API
UU
VV
LL
SANDPIT
200
100
SPRINGS
AAA
A'
Chippewa Creek
N
LANDFILL
MARSH ROAD
50
100
150
200
SANDPIT
SPRINGS
Chippewa Creek
0
100
300
500
metres
0
200
400
800
1200
1600
feet

Figure 1. Plan view of the North Bay Landfill Leachate Plume. The maximum chloride (left) and TOC (right) concentrations at each multilevel piezometer for 1982 are contoured.

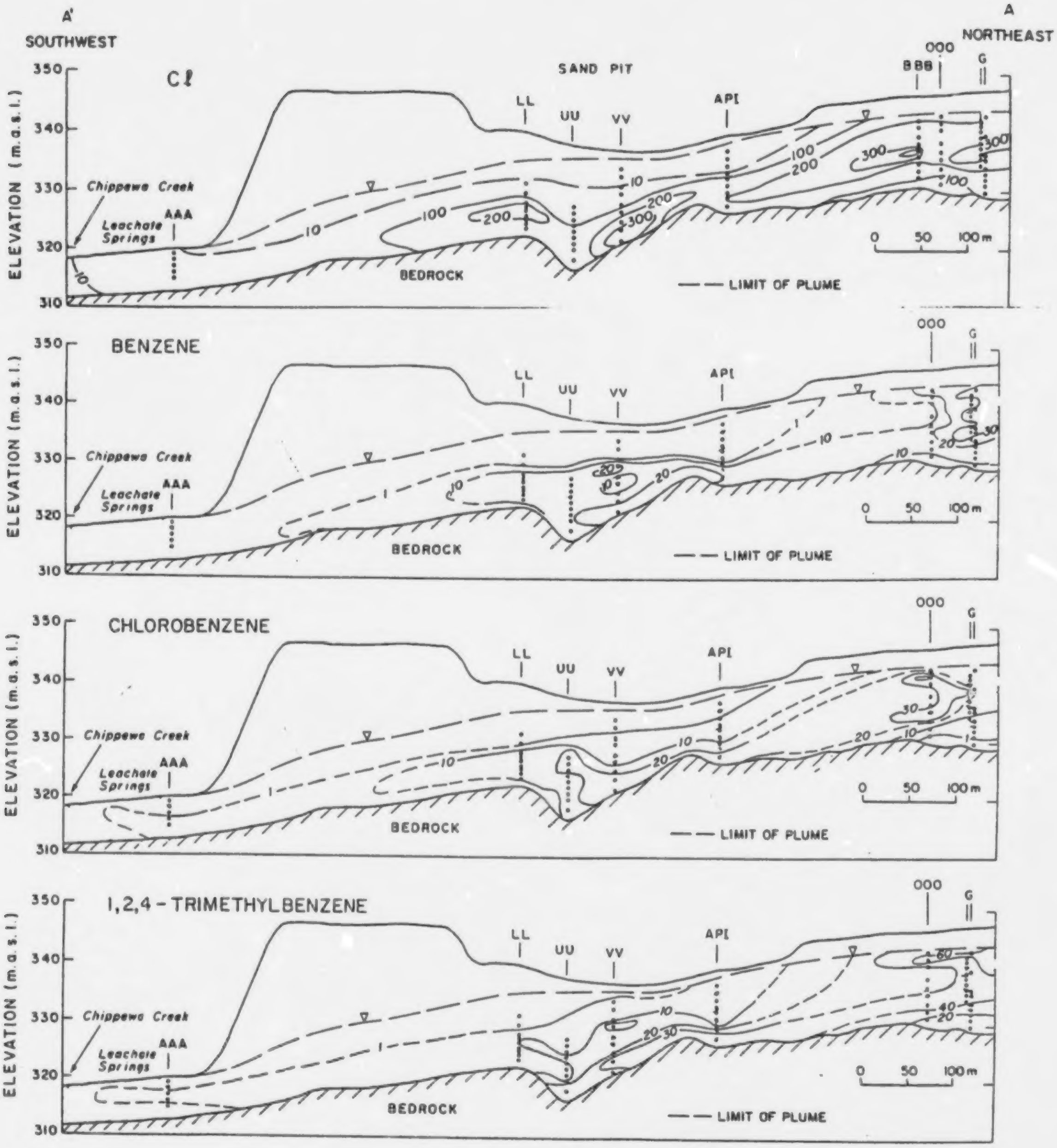
A'
SOUTHWEST
A
NORTHEAST
Cℓ
SAND PIT
BENZENE
CHLOROBENZENE
1,2,4 - TRIMETHYLBENZENE
ELEVATION (m.a.s.l.)
350
340
330
320
310
Chippewa Creek
Leachate Springs
AAA
LL
UU
VV
API
BBB
OOO
G
BEDROCK
LIMIT OF PLUME
0
50
100m
10
100
200
300
1
20
30
40
60

Figure 2. Chloride, benzene, chlorobenzene and 1,2,4-trimethylbenzene distributions along cross-section A-A'. Contoured from July, 1985 data.

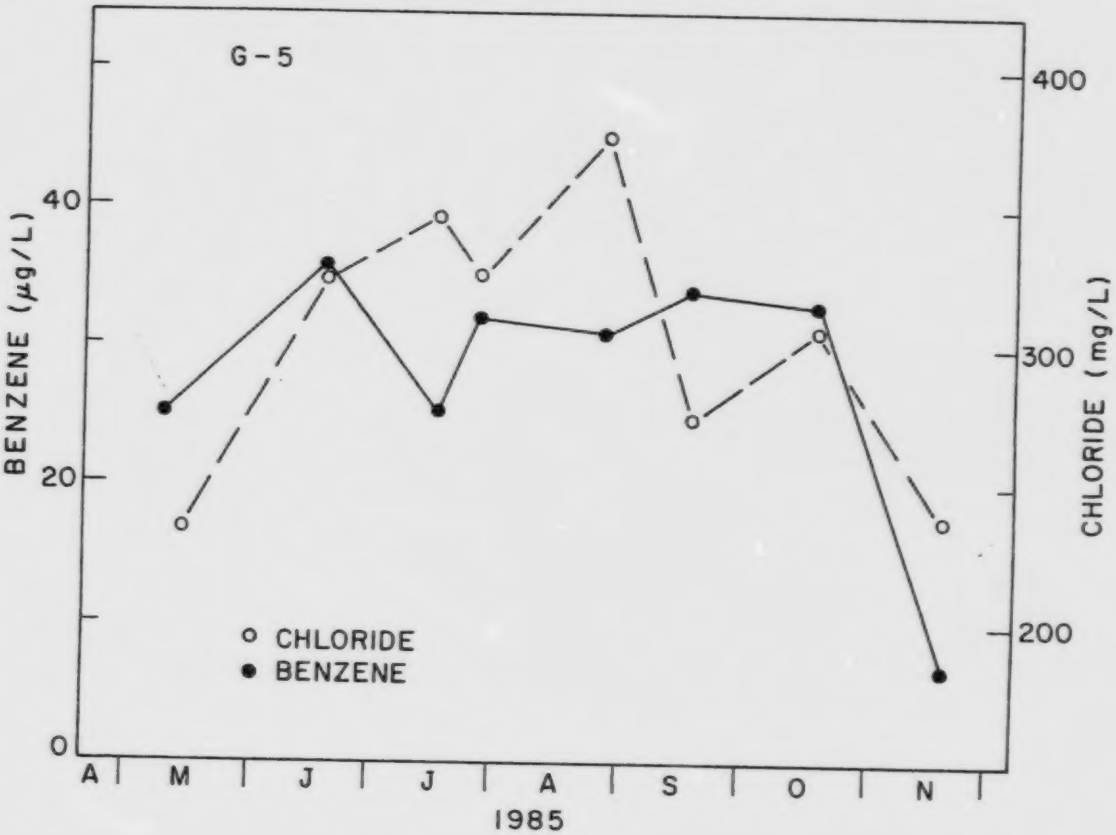

Figure 3. Temporal variation (1985) for chloride and benzene concentrations in groundwater from piezometer G-5, near the landfill.

DISPERSION OF THE STOUFFVILE CONTAMINANT PLUME

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DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME

Introduction

The Oak Ridges aquifer complex is a source of large quantities of high quality water. These sand and gravel aquifers underly much of the Oak Ridges moraine on which the Stouffville landfill site is located (Fig. 1). Variations in groundwater quality parameters over the years show that a plume of contamination has developed in the aquifer under the landfill. The objective of this paper is to describe the complex physical and hydrogeological setting at this site and begin to interpret the observed variations in groundwater quality caused by plume evolution.

Waste disposal activities

Operations at the landfill site began in 1962. No accurate records of the nature or the quantity of wastes disposed of at the site are available before 1974. However, some facts are known about disposal activities at the site in the early years. Both liquid industrial wastes and solid wastes were received until 1970. The liquid wastes were disposed of on top of the solid wastes and covered with earth in the south and southwest areas. Natural depressions formed by glacial processes were also used for the disposal of liquid wastes (Fig. 2). After 1970 only solid municipal wastes were accepted at the site. The depressions used for liquid waste disposal were filled with solid wastes in 1973-74 and then buried by waste and cover material. The site was closed in July 1985 after millions of tons of waste had been received.

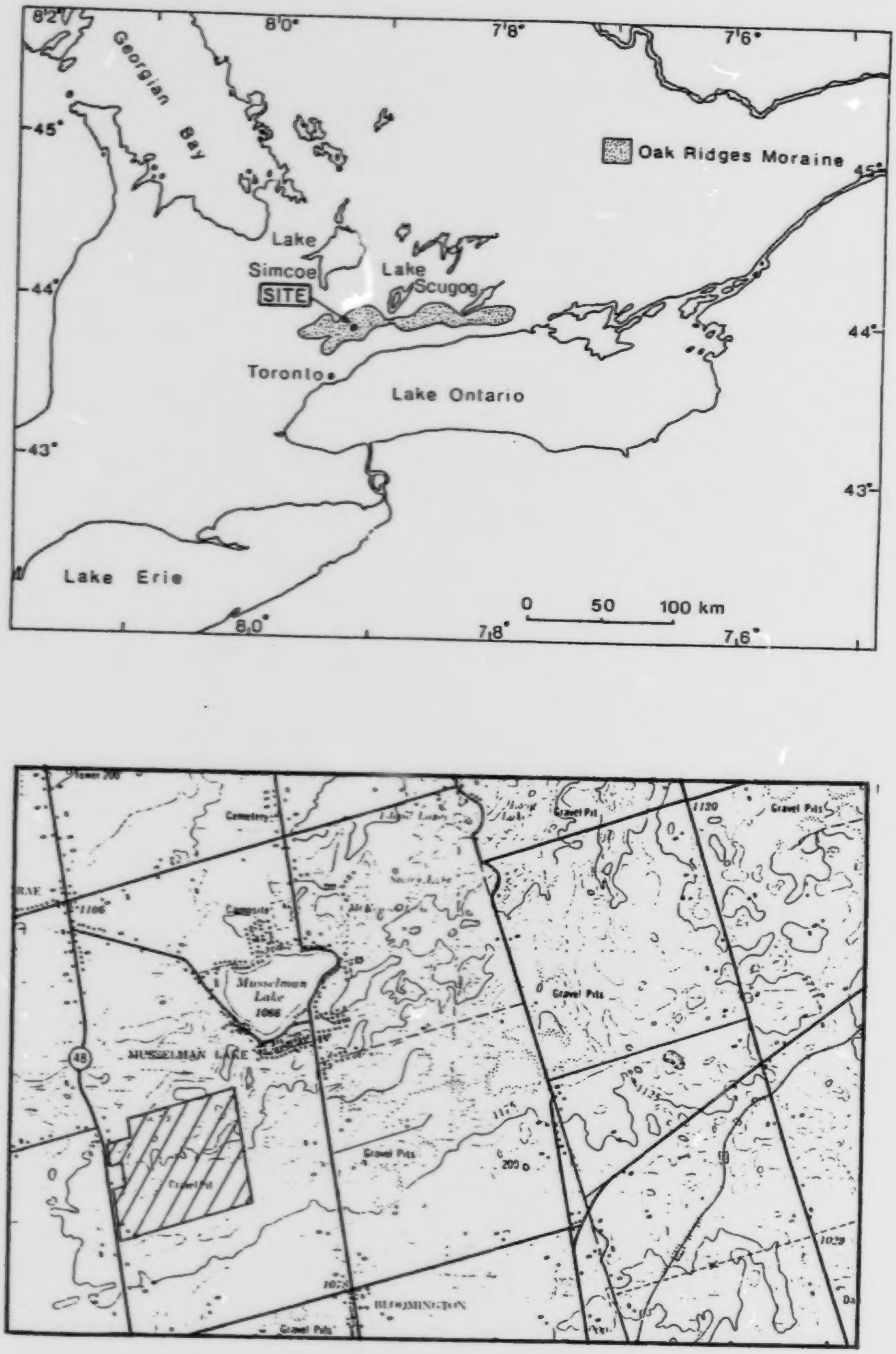
82°
80°
78°
76°
45°
44°
43°
Georgian Bay
Oak Ridges Moraine
Lake Simcoe
Lake Scugog
SITE
Toronto
Lake Ontario
Lake Erie
0 50 100 km
Cemetery
Campsite
Musselman Lake 1066
MUSSELMAN LAKE
48
Gravel Pits
Gravel Pit
1120
1125
200
1029
BLOOMINGTON

Figure 1: Location map

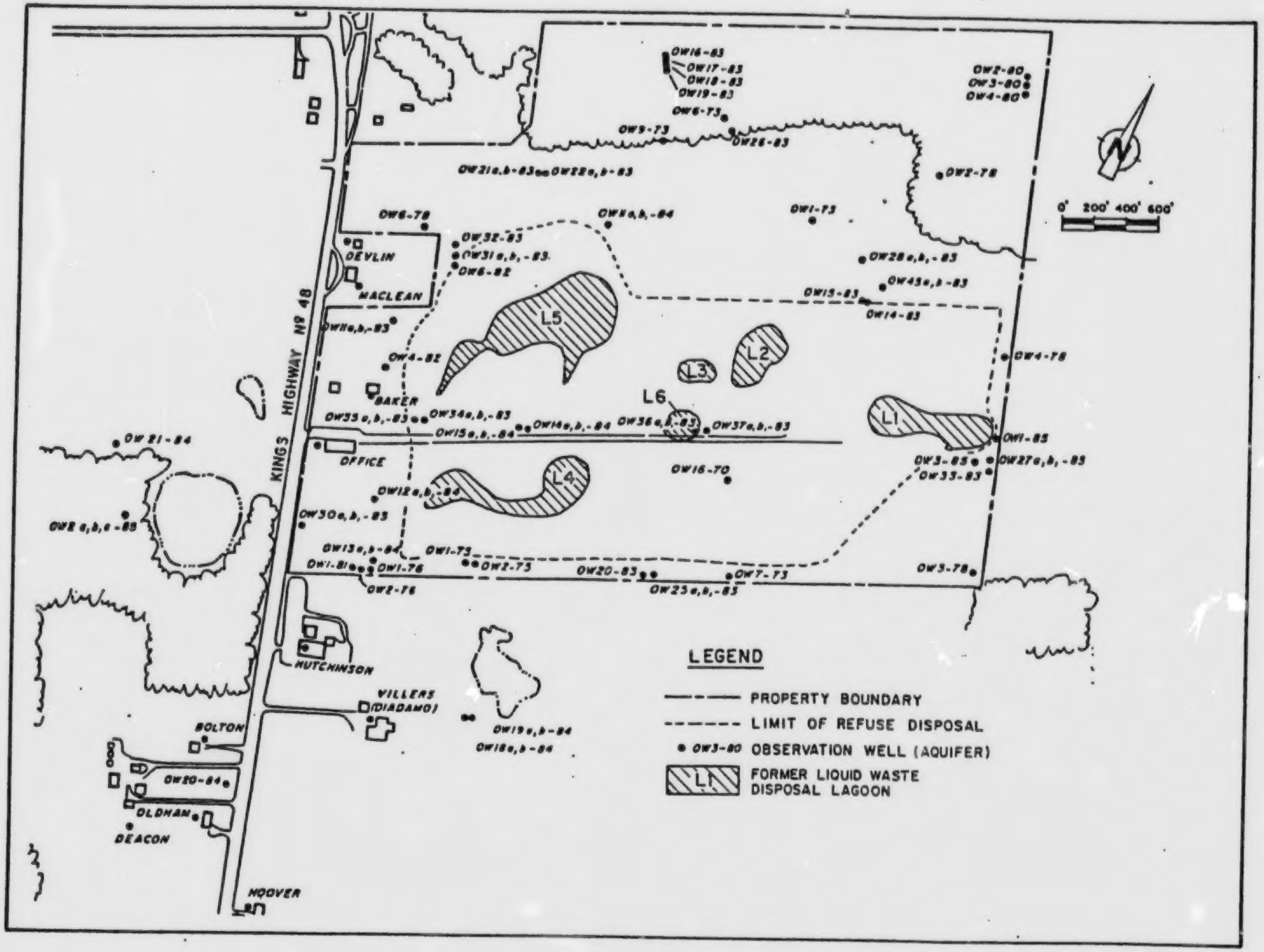
KINGS HIGHWAY Nº 48
OW16-83
OW17-83
OW18-83
OW19-83
OW6-73
OW9-73
OW26-83
OW2-80
OW3-80
OW4-80
OW21a,b-83
OW22a,b-83
OW2-78
OW1-73
OW6-78
OW11a,b,-84
OW32-83
OW31a,b,-83
OW6-82
DEVLIN
MACLEAN
OW28a,b,-83
OW43a,b-83
OW15-83
OW14-83
OW11a,b,-83
L5
L2
L3
L6
L1
L4
OW4-78
OW4-82
BAKER
OW35a,b,-83
OW34a,b,-83
OW15a,b,-84
OW14a,b,-84
OW36a,b,-83
OW37a,b,-83
OW1-85
OW21-84
OFFICE
OW3-85
OW27a,b,-85
OW33-83
OW16-70
OW12a,b,-84
OW30a,b,-83
OW8a,b,c-85
OW13a,b-84
OW1-73
OW1-81
OW1-76
OW2-73
OW20-83
OW7-73
OW3-78
OW2-76
OW25a,b,-85
HUTCHINSON
VILLERS (DIADAMO)
OW19a,b-84
OW18a,b-84
BOLTON
OW20-84
OLDHAM
DEACON
HOOVER
N
0' 200' 400' 600'
LEGEND
PROPERTY BOUNDARY
LIMIT OF REFUSE DISPOSAL
OW3-80 OBSERVATION WELL (AQUIFER)
L1 FORMER LIQUID WASTE DISPOSAL LAGOON

Figure 2: Aquifer observation wells and disposal lagoons

(Modified from WMI, 1985)

Quaternary Geology

A recent study in the Musselman Lake area (Kaye, 1986) led to an improved understanding of the local depositional history and hydrostratigraphy.

Advances and retreats of Late Wisconsinan glacial ice are responsible for the different types of deposits formed in the area. Till units were formed during ice advances, while retreats resulted in deposition of outwash sands and gravels.

The first record of glacial advance is the group of tills and glaciolacustrine units observed in the deepest holes on site. The sand and gravel aquifers underlying the site was formed during the subsequent ice retreat. A second ice advance followed and generated the fine grained Halton till, south of Musselman Lake. An unconfined glacio fluvial aquifer was formed to the north of Musselman Lake during the last ice retreat. See Figure 3 for illustration of simplified stratigraphy of the area.

Site description

Previous investigations of the site (WMI, 1985) used logs from observation wells and borehole resistivity logs from 17 deep holes to define the hydrostratigraphy under the site. Five units were identified.

The uppermost unit is thin and discontinuous in the north part of the site, but reaches a 20 m thickness to the west. The composition of this sediment, known as the Halton till, varies from a very clayey to a very sandy silt diamict. Hydraulic conductivity values of 1 x 10^{-2} to 3 x 10^{-7} cm/s were obtained from grain size analyses using the Hazen method. This wide range illustrates the diversity of materials forming the unit. Local perched water table systems are found associated with the impermeable material, but at several places, the Halton till is unsaturated throughout.

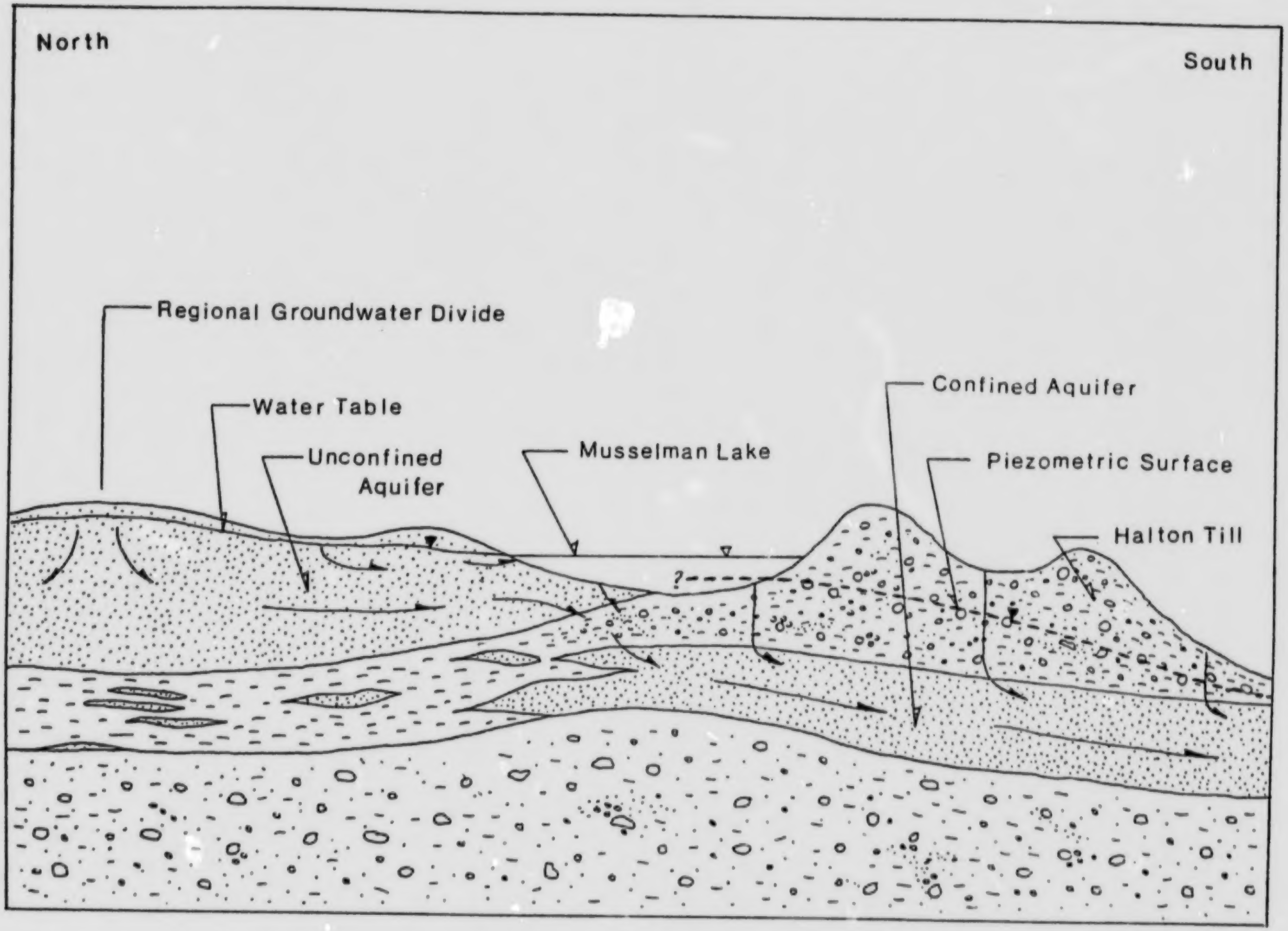
North
South
Regional Groundwater Divide
Water Table
Unconfined Aquifer
Musselman Lake
Confined Aquifer
Piezometric Surface
Halton Till
?

Figure 3: Local stratigraphy and flow pattern

(From Kaye, 1980)

Below the Halton till is the main sand aquifer of glacio fluvial origin. This heterogeneous unit consists of beds and lenses of clay, silt and gravel in fine to medium grained sand. The 30 to 60 m thick aquifer is unconfined in the northernmost part of the site, but is overlain by the Halton till over the remainder of the site, and elsewhere in the region. A thick unsaturated zone occurs between the Halton till and the water table under the site.

Three fine-grained deposits acting as aquitards underly the aquifer at different places below the site and for practical purposes, represent the bottom of the flow system.

Hydrology of the Halton till

Driller logs of holes penetrating the Halton till show highly variable stratigraphy. These complex conditions result in different infiltration rates over the site. Some observations are indicative of generally impermeable conditions: thick unsaturated zone, numerous locations of ponding and perched water, and very stable aquifer well hydrographs. Conversely, the existence of some permeable areas is indicated by a minimal amount of runoff from the site before it was altered, and the rapid infiltration of the liquid wastes in the disposal 'lagoons'. Also, several dry zones occur in the unit, indicating recharge conditions.

Comparison of hydrographs and water quality data for shallow wells suggest poor hydraulic connections between the local zones of perched water in the Halton till. Strong vertical gradients and discontinuity of the perched groundwater zones in the till (Fig. 4) are good evidence that the hazard for off site contamination through the Halton till is minimal.

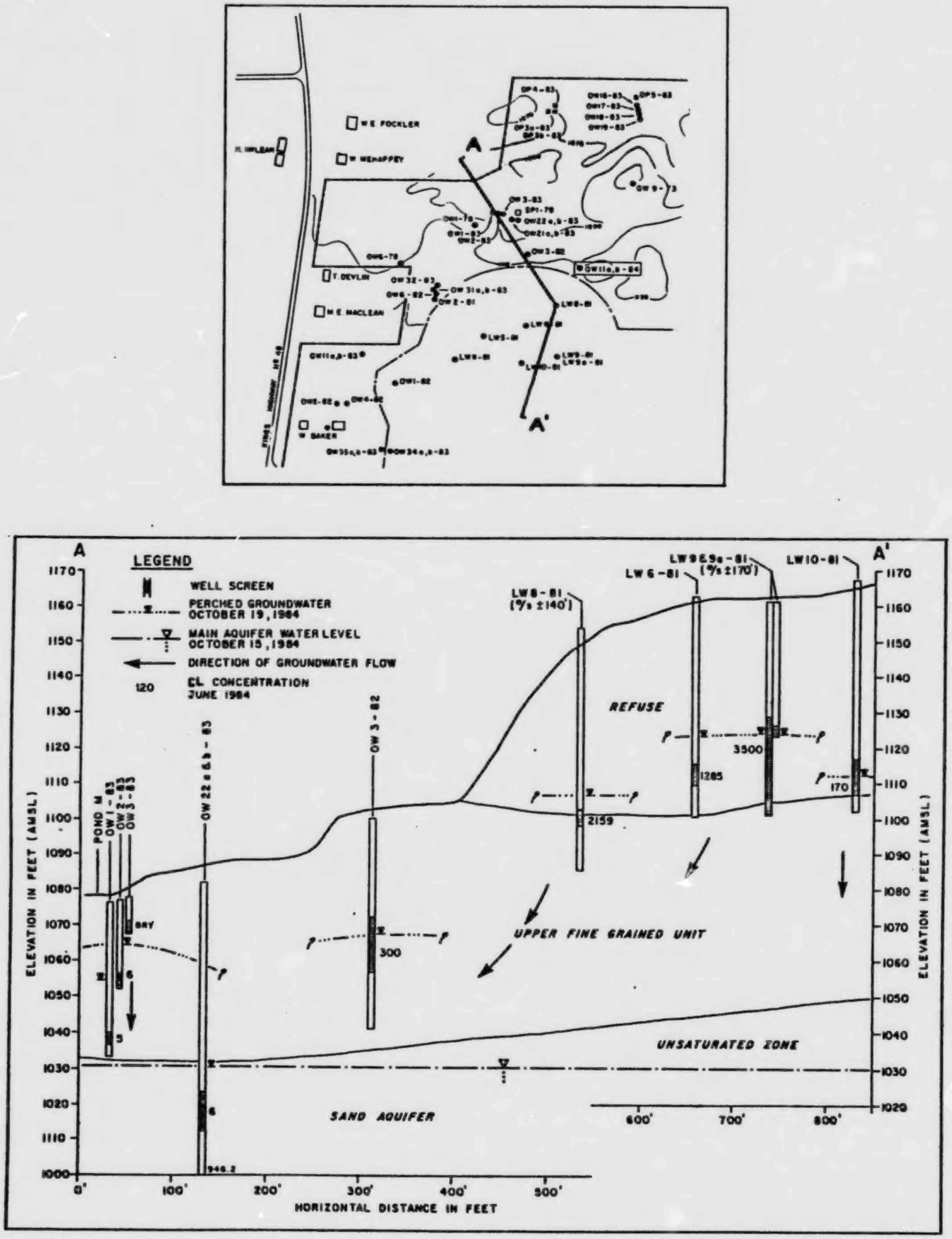
A
A'
W.E. FOCKLER
W. MEHAFFEY
T. DEVLIN
W.E. MACLEAN
W. BAKER
LEGEND
WELL SCREEN
PERCHED GROUNDWATER OCTOBER 19, 1984
MAIN AQUIFER WATER LEVEL OCTOBER 15, 1984
DIRECTION OF GROUNDWATER FLOW
120 CL CONCENTRATION JUNE 1984
LW8-81 (T/s ±140')
LW6-81
LW9 & 9a-81 (T/s ±170')
LW10-81
OW 3-82
OW 22 a & b - 83
POND M
OW 1-83
OW 2-83
OW 3-83
DRY
REFUSE
UPPER FINE GRAINED UNIT
UNSATURATED ZONE
SAND AQUIFER
3500
1285
2159
170
300
6
5
6
946.2
ELEVATION IN FEET (AMSL)
HORIZONTAL DISTANCE IN FEET
0'
100'
200'
300'
400'
500'
600'
700'
800'
1000
1010
1020
1030
1040
1050
1060
1070
1080
1090
1100
1110
1120
1130
1140
1150
1160
1170

Figure 4: Perched water in the north slope

(Adapted from WMI, 1985)

Flow in the main aquifer

Regional groundwater flow is to the southwest with a regional horizontal hydraulic gradient on the order of 0.012 (WMI, 1985). In places directly under the site values as low as 0.004 are observed.

Kaye (1986) came to the conclusion that Musselman Lake was receiving recharge from the northern unconfined aquifer, while acting as a reservoir to the southern aquifer. This constant source of recharge to the southern aquifer, augmented by infiltration from land surface, maintains the mass flux between the landfill and the site through the year.

Equipotentials configuration on site fluctuates seasonally and indicates local recharge. A depression for storage of storm water at the northeast corner of the property acts as one obvious recharge zone (Fig. 5).

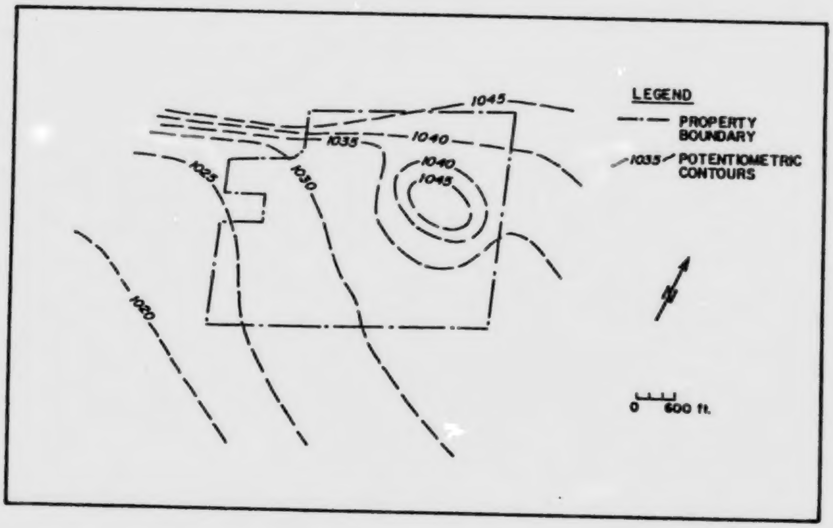
1045
1035
1040
1040
1045
1025
1030
1020
LEGEND
PROPERTY BOUNDARY
1035
POTENTIOMETRIC CONTOURS
N
0
600 ft.

Figure 5: Isopotentials in main aquifer

(October, 1984)

During the spring, circular isopotentials of a water table mound can be drawn under this zone. In the winter the mound decays and isopotentials have a curvilinear shape. This recharge mound has a strong, although temporary, influence on the direction of groundwater flow in the main aquifer, disrupting the normal flow pattern and producing off site gradients that must be considered in an analysis of contaminant migration.

Monitoring program

In the period from 1970 to 1985, 96 observation wells, 25 test holes, 22 boreholes, and 21 leachate wells were installed at the site. The main aquifer was penetrated by 38 of these installations consisting of standpipe piezometers or nests of 2 or 3 piezometers spread over the aquifer thickness. Ten domestic wells are located on or very close to the site. The earliest groundwater quality data were obtained in 1968 from the Hutchinson domestic well, and at that time chemical analyses were limited to chloride, conductivity, phenols and sulphate.

In November 1981, a university laboratory reported bacterial mutagenicity in the water of a private well adjacent to the landfill site. This brought about the initiation by the Ministry of the Environment (MOE) in December 1981 of an in-depth chemical and biological study of the site. The final report was completed in November 1982 and no bacterial mutagenic activity was identified. It was also concluded that there were no evidence of off site contamination by the industrial organics present in the landfill (MOE, 1982).

From 1982 to 1984 a hydrologic investigation was conducted by Conestoga Rovers and Associates for the site owner, WMI, as a condition for completion of activities and closing of the landfill site. The resulting report is available at the MOE and the Town of Stouffville. Since the initiation of that study, a monitoring program in which some 50 points are sampled every three months is being conducted. The water samples are analyzed for selected indicator parameters.

Discussion

The Halton till on the site contains the refuse, and thus considerable contamination. This contamination may be reaching the main aquifer, but it does not appear to migrate significantly off site in the local perched water systems of the till unit.

No generalization can be made concerning the hydraulic properties of the Halton till, except that they are highly variable at the site. As an alternative to an impracticle attempt to characterize infiltration rates through the Halton till, this unit at the site is considered as a potential contaminant source whose impact would first be recorded at the water table of the main aquifer. Therefore the contamination reaching the water table is treated as the contaminant input function to the flow system. The regional groundwater flow system and main aquifer characteristics under the site have been determined. Plumes of contamination in the main aquifer can be drawn (see Fig. 6), and studies to delineate the exact configuration and size are in progress.

Two different hypotheses as to the cause of the observed historical water quality variations exit. Consecutive peaks observed in wells at increasing distance from the lagoons are seen as evidence of the fast migration of water contaminated by liquid wastes. The graph of historical chloride concentration variations has the same general shape as the arrival curve of a dispersed contaminant front. A different interpretation would be that the liquid waste produced these historical chloride arrival curves, and their peaks. Preliminary computer simulations of this possibility were performed using an analytical solution for 2-D transport from a

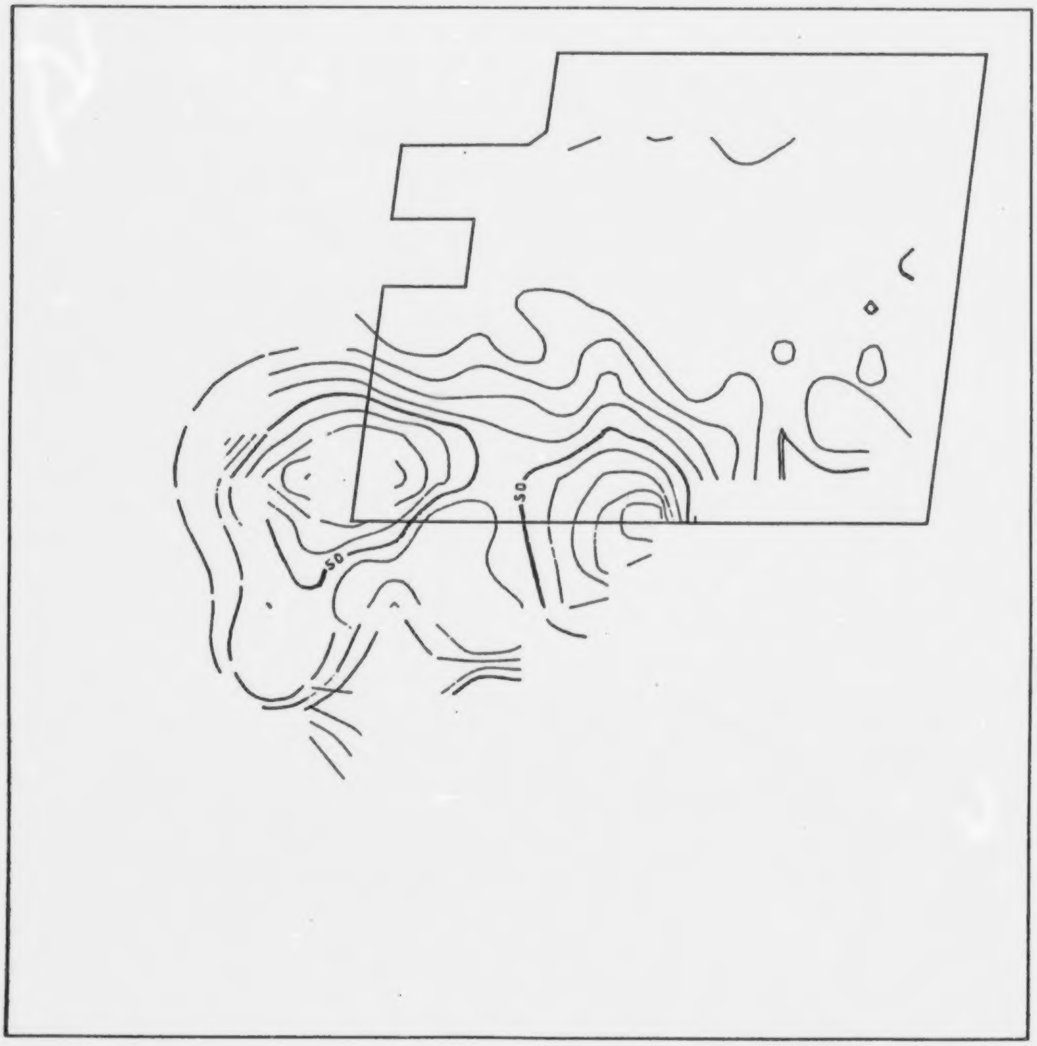

Figure 6: Chloride plume in main aquifer

May 1985 - Contour interval of 10 mg/l

line source (Sudicky, 1986). The regional dispersivity value of 20 observed in glacial deposits of Long Island (Anderson, 1979) was used. A relatively small velocity of 25 m/y was required to simulate the historical curves. The general shape of the observed curve, and its time span between first arrival of concentrations higher than background and a relative stabilization of concentration could be reproduced at different locations.

Historical water quality variations reach a relative level of stability. The record of water quality variations in the younger wells (1983-85) is shorter, but values of the indicator parameters seem relatively stable. The volume of aquifer of concern is quite large, and uncertainties about the degree of control on the plume can be raised, but up to date observations do not reflect fast off site plume migration.

Three-dimensionnal computer simulations of variable to constant in time inout at the water table would help to understand how the contamination plume has developped.

Conclusions

The regional and local hydrogeologic environment of the landfill site have been described. No significant off site contaminant migration occurs in the Halton till. The till is generally impermeable, but permeable pathways exist under the site resulting in contamination of the main aquifer. Up to date results from the monitoring program indicate that the plume of contamination does not extend far from the site.

The drilling of additional holes in the main aquifer is planned for this year to increase control on plume delineation. More work on the chemical data base is in progress to determine the proce sses influencing plume development. More involved transport modelling will be accomplished.

References

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DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL COLLECTION OF LEACHATE UNDER SANITARY LANDFILLS

SUBMITTED TO:

Research Advisory Committee
Ontario Ministry of the Environment
135 St. Clair Avenue West, 12th Floor
Toronto, Ontario
M4V 1P5

SUBMITTED BY:

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N2L 3G1

NOVEMBER, 1986

DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS

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ABSTRACT

A two-dimensional finite element model was used to study the effectiveness of tile drain systems for capturing leachate under unlined sanitary landfills. Computed steady-state conditions were compared with data produced from a laboratory model. Simulations were conducted for a simplified drain system with varying vertical hydraulic gradients, drain depth, thickness of the flow field, drain spacing, and leachate production rate. Results showed that most of the leachate can be collected if an upward vertical gradient exists beneath the drain level. If the vertical gradient is downward, the drains have to be very closely spaced in order to collect the leachate. Drain performance depends on the rate of recharge of leachate into the system, which partly controls the height of the groundwater mound between the drains. Optimal conditions can be attained when all the leachate is collected with minimum infiltration of groundwater coming from depth.

Introduction

In humid and sub-humid regions, the production of leachate is an inevitable consequence of the interaction of infiltrated water with buried waste. Leachate characteristically contains concentrations of dissolved matter far in excess of drinking water standards. Preventing the contamination of groundwater by landfill leachate is a major consideration in landfill design. The key factor in avoiding serious contamination is the proper placement of the landfill, which should be done by taking in account the groundwater flow directions, the hydrogeological properties of the subsurface materials and the proximity of aquifers and surface water bodies. In addition, the leachate production rates have to be evaluated and controlled. A common practice to achieve this is by the use of leachate collection systems placed at the bottom of the landfill. These systems are usually composed of drain networks. In many cases, clay liners are used to hydraulically isolate the landfill from the underlying geological material.

Several mathematical models to evaluate the effectiveness of leachate collection are available in the literature. However, these models were not developed for cases where, in order to avoid the high costs of liner construction, proposed leachate collection systems consist solely of a tile drain network.

The purpose of this study is to determine a method suitable to evaluate the efficiency of tile drain systems for collecting leachate without the use of liners. The work described is part of a three year research project funded by the MOE lottery fund. In a previous report (Farvolden et al., 1985) experiments with a laboratory model were described. Parallel to these experiments, a two-dimensional finite element numerical model was applied to a simple system similar to the one modelled in the laboratory. Results of this work were summarized in Abdul et al. (1985). The present report discusses the results produced by the two previous studies and describes the progress made towards the application of the numerical model to more general hydrogeological situations.

MATHEMATICAL MODELS TO EVALUATE LEACHATE COLLECTION

Figure 1 shows three different leachate collection system geometries studied in the literature. For a horizontal clay liner of zero permeability (Figure 1a), the following equation from Harr (1962) has been used to describe the shape of the groundwater mound on top of the liner:

$$h = (R/K\ (L - x)\ x)^{1/2}$$

where L is the distance between the drains, K is the horizontal hydraulic conductivity of the drained medium, R is the steady-state rate of leachate input into the system, and x is the horizontal distance from the drains. From this equation, it can be shown that: (1) the maximum height of the water table above the level of the tile drain increases as the recharge increases and/or the hydraulic conductivity decreases, and (2) the maximum height of the water table increases as the distance between the drains decreases.

McBean et. al. (1982) derived an equation for a sloped liner (1b) and presented a case study where the concern is the change of height of the groundwater mound for different steady-state recharge fluxes. McBean et al. (1982) suggested the use of their model to study alternative designs of leachate collection systems with respect to drain spacing and groundwater mounding.

An elaborate attempt to study the design of leachate collection systems is the one by Wong (1977). He developed equations to approximate the movement of a volume of water moving over the surface of a sloped clay liner towards a collector tile (figure 1c). Leakage through the liner and collection efficiency are expressed as a function of liner slope (θ), liner thickness (d), leachate head buildup (h), leachate flow distance (S), and hydraulic conductivities of the liner (K_2) and the material overlying it (K_1). Wong's model has been used for many practical design problems. His assumptions were:

1. The drainage layer overlying the clay liner has the same hydraulic conductivity as the refuse material
2. All materials are at field capacity, so that any infiltration of precipitation is transmitted to the bottom of the landfill
3. Pressure in the drain is zero
4. The leachate collection system is above the water table. Any effect of groundwater flow under the liner is neglected.
5. Leachate buildup appears instantly over the liner. The leachate saturates a rectilinear volume above the liner, and retains this shape while draining towards the collection drain and through the liner.

Kmet et. al. (1981) examined closely each one of Wong's assumptions and presented a sensitivity analysis based on Wong's model. They also presented a refinement of the method to estimate the value of the head buildup (h) after multiple recharge events. Dematrocopoulis et. al. (1984) give the most recent review of leachate collection models. They considered assumptions (1) and (5) of Wong to be controversial and presented a sensitivity analysis based on Wong's model, with modifications for time-variable leachate productions. Moore (1980) obtained leakage through the liner using Richard's equation for variably saturated flow. He also presented a methodology for evaluating the performance of leachate collection systems with liners.

In the case of leachate collection systems that do not include the low permeability liner, the natural hydrogeological conditions occuring under the landfill become important, and assumption 4 of the Wong model might not be applicable.

REVIEW AND DISCUSSION OF PREVIOUS WORK

Figures 2 shows a simplified view of what the hydrogeological conditions beneath the landfill might be. The landfill rests in a low permeability surface unit (clay or till) which overlies a second unit of higher permeability (aquifer). The flow system around the drains can be simplified to a 'half cell'. Figures 3 and 4 show the definition of the boundary conditions for the half cell system and the experimental apparatus used for the laboratory study. (Abdul et al., 1985, and Farvolden et. al., 1985). Table 1 defines the different parameters and dimensionless ratios that were used to study the half cell. In defining the system, the following assumptions were made:

1. The hydraulic conductivity of the landfill is the same as the hydraulic conductivity of the underlying porous medium.
2. All material beneath the drain level is saturated. The drains are thus below or at the natural water table level.
3. Recharge of leachate reaching the level of the drains is at steady state and is constant.
4. Any effect produced by the unsaturated zone above the drains is neglected.
5. Pressure in the drain is zero.
6. All flow occurs in a plane. Because a symmetrical flow field exists between the drains, no flow takes place across the side boundaries of the cell.

7. The landfill is built in a low permeability hydrogeological unit overlying an aquifer. This causes the hydraulic head at a certain depth beneath the landfill to be constant.

Both laboratory and numerical models of the half cell system were used to analyse the flow field around the drain by verifying the sensitivity of the flow field to changes in the values of recharge (R), hydraulic conductivity (K), hydraulic head at depth and at the drain (Ha,Hd) and half spacing between the drains. The results were presented in the form of response curves showing the variation of the value of Qa/Qr relative to dimensionless ratios R/K, Ha/Hd and Hd/L (figure 5). Qa is the total resulting discharge of water at the bottom of the system and Qr is the input discharge of leachate. Fluxes entering the system were considered positive and those leaving the system, negative. Consequently, the response factor Qa/Qr is related to the degree of leachate collection in the following way: as Qa/Qr increases (becomes more positive), leachate collection increases; as Qa/Qr decreases (becomes more negative) collection decreases.

The response curves show that leachate collection is higher in cases of upward vertical gradients (Ha/Hd>1) than in cases of downward gradients (Ha/Hd<1). In cases where vertical gradients are directed downward, the collection increases as R/K increases. When vertical gradients are directed upward, leachate collection increases as R/K decreases. In the particular case where no vertical gradients exist, leachate collection is only slightly dependent on changes in values of recharge or hydraulic conductivity.

A large positive value of Qa/Qr indicates that a large amount of water is infiltrating from the lower layer into the half cell system. The flownets of figure 6 are useful to visualize the different scenarios that can occur. In figure 6a, the ratio Ha/Hd is smaller than one, and most of the leachate is escaping through the bottom of the system. Figure 6b shows the conditions occuring when Ha/Hd equals 1.10: approximately half of the leachate is collected.

At least some of the leachate bypasses the drains in all the cases where Qa/Qr is smaller than zero. Figure 6c shows a situation that occurs when Qa/Qr is positive: most of the leachate is collected, but there is also a significant amount of water infiltrating from the bottom of the system. In this case, the value of Qd is equal to the sum of the discharge of water coming from the aquifer (Qai) and the discharge of leachate that is intercepted (Qdr). The value of Qai is important in the assessement of drain performance because infiltration of uncontaminated water increases the volume of fluid to be processed by the drainage system, therefore increasing operation costs.

On figure 7, the discharge ratios Qai/Qr, Qao/Qr, and Qdr/Qr are plotted along with the response curve for values of Hd/L of 0.75 and Ha/Hd of 1.10. Points A and C correspond to situations illustrated by the flownets of figure 6. Zone I of the response curve ($R/K < 0.03$) includes all situations where the flow field in the half cell is dominated by infiltration through the bottom boundary. Zone III ($R/K > 0.08$) includes situations where leachate is bypassing the drain with no infiltration from the bottom. Zone II ($0.03 < R/K < 0.08$) is the 'transition' zone where, at the bottom, flow occurs in both directions. From the relations between the different curves on figure 7, it can be seen that for:

zone I: Qa = Qai, Qao = 0

zone II: Qa = Qai + Qao

zone III: Qa = Qao, Qai = 0

Figure 8 shows the flow conditions occuring at point D of figure 7.

Optimization of the half cell system.

The efficiency of the leachate collection system will be highest when a maximum amount of leachate is intercepted and a minimum amount of water from depth is collected. For the response curve shown on figure 7, optimal drainage conditions will occur near point B.

It has to be understood that the conditions occuring at point C (and illustrated in figure 6c) are very unstable. Variations of any of the parameters due to transient effects could mean important changes in the flow conditions. Consequently, before concentrating efforts on developing an exact optimization procedure based on the half cell system, it is necessary to examine carefully the applicability of its assumptions to real-life situations. This is the object of present research for which preliminary work is described at the end of this paper.

COMPARISON BETWEEN LABORATORY AND NUMERICAL RESULTS.

The purpose of the laboratory experiments was to verify the results of the numerical model for simple hydrogeological conditions. The laboratory sand medium was originally assumed to be homogeneous and isotropic, with a hydraulic conductivity value of 4.18×10^{-3} cm/s. Figure 9 compares response curves from the laboratory and numerical models for values of Ha/Hd of 1.06 and Hd/L of 0.64. It can be seen that although the curves show the same trend, there is a significant difference in the values of the parameters. Three possible causes for the difference were considered: Numerical error, anisotropy in the laboratory sand medium, and error in the definition of the boundary conditions.

The best fit on figure 9 was produced using an anisotropy value (Kx/Ky) of 2. The elimination of the other possible causes lead us to believe that the difference in the laboratory and the numerical results was due to uneven packing of the laboratory porous medium which produced a slight anisotropy. The presence of inhomogeneities are also likely, and might be the cause behind the remaining difference between the curves of figure 9.

Although the results of the numerical model did not match perfectly the ones produced by the laboratory model, the good agreement between the trends of the two sets of results is sufficient to justify the use of the numerical model for more complex situations.

NON HOMOGENEOUS HALF CELL SYSTEMS

The effect of a layer of lower hydraulic conductivity on the half cell flow system was studied, with resulting flownets such as the one in figure 10. Figures 11, 12 and 13 show the effect of layer depth (d), thickness (b), and hydraulic conductivity contrast (K_1/K_2) on the response of the system. For the conditions tested in figure 11, the value of the response factor slightly increased with the depth of the layer for depths smaller than 4 m. If the layer was located deeper than 4 m, a change in depth did not affect the flow system.

Figure 12 shows the effect of layer thickness on the flow system. All other conditions remaining constant, an increase in layer thickness of up to 2 m. had a significant effect on the system. The decrease in Qa/Qr with an increase in thickness in the case where Ha/Hd = 1.15 was observed because the low permeability layer was preventing aquifer water from infiltrating into the system. The flow system was independent of layer thickness at values of thickness greater than 2 m. Figure 13 shows the effect of the conductivity contrast on the response factor. The hydraulic barrier effect produced by the low conductivity layer is reflected by the convergence of the response curves towards Qa/Qr = 0.

EFFECT OF DRAINAGE ON THE REGIONAL FLOW SYSTEM

In order to evaluate the conditions exterior to the half cell system, and to examine the effect of landfill drainage on a regional scale, flow systems such as the one shown on figure 14 are presently being studied. The system is homogeneous and lies on an impermeable base. It is recharged from the top at a constant, steady state flux of 20 cm/y. Recharge is also occurring through the left boundary (upflow) at a rate equal to the total recharge to the top that accumulates over a distance of 1000 m upstream from the left boundary. The hydraulic conductivity is equal to 0.1 cm/s. The right boundary is set at a constant head of 50 m. The water table position is found by iteration, and is plotted in exaggerated scale over the cross section. The length of the section is 1000 m and its thickness is 50 m. Drainage is represented by the introduction of a constant head node along the top boundary, 30 cm below the natural water-table. It is assumed that the pressure in the drain is zero and that the water table draws down to the drain. It can be seen on figure 14 that a component of horizontal flow exists in all of the streamlines leading to the drain section. The half cell system cannot be used to describe these drainage conditions because assumption 6 stating that no flow takes place across the side boundaries of the cell does not hold. Because the flow system of Figure 14 lies on an impermeable base, it represents an extreme case. If leakage was to occur down into a lower hydrogeological unit, a stronger vertical component of flow would appear.

Figure 15 shows equipotential lines for a system in which flow is mainly vertical. The bottom layer has the same boundary conditions as the system in figure 14. The ratio of hydraulic conductivities between the top and the bottom layer is 10^{-5}. Recharge to the top occurs at a steady state rate of 20 cm/y, and the lateral boundaries for the top layer are assumed to be impermeable. In this section, a groundwater divide exists on each side of the drain, and the potential at depth is nearly constant. Half cell assumptions 6 and 7 are valid and the half cell theory applies.

CONCLUSION

For landfills located on low permeability material overlying aquifers, the half cell approach might be a useful tool for the evaluation of leachate collection systems. Figure 15 shows how the zone located under the landfill can be divided into sections suitable for the application of the half cell model. In section A, symmetry boundaries exist under the drains and at mid-distance between them, thus defining the lateral limits of the half cell. Along the edge of the landfill, a symmetry boundary occurs between the vertical flow section (C) and the drain flow section (B), thus defining the limits of a second cell. The results of a sensitivity analysis presently under way will determine the type of conditions necessary for the situation described in figure 16 to occur. Work on a method to evaluate the drainage conditions in cases where horizontal flow occurs is also in progress.

ACKNOWLEDGEMENTS

The financial support from the Ontario Ministry of the Environment is gratefully acknowledged.

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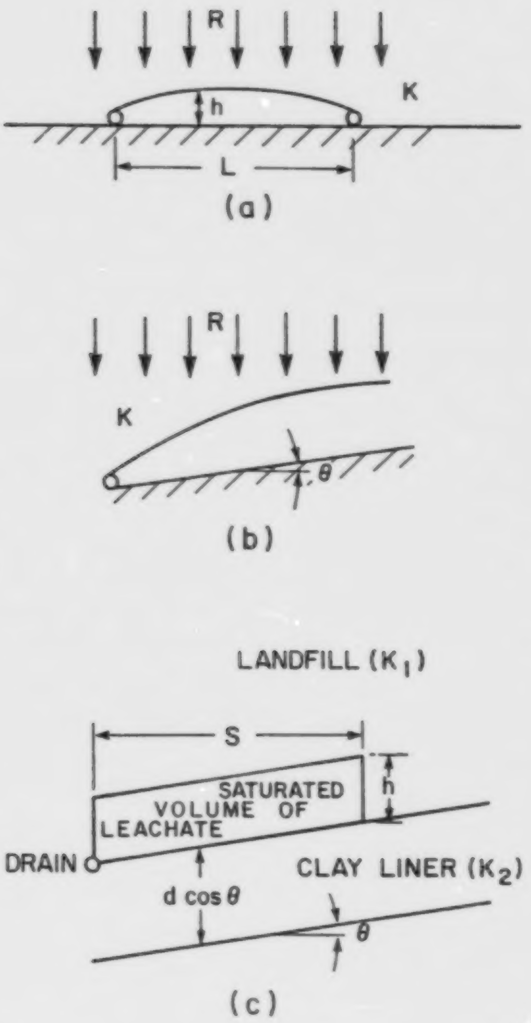

R
h
K
L
(a)
R
K
θ
(b)
LANDFILL (K_1)
S
h
SATURATED VOLUME OF LEACHATE
DRAIN
CLAY LINER (K_2)
d cos θ
θ
(c)

Figure 1. Three different leachate collection system geometries studied in the literature: (a) horizontal liner of zero permeability (Harr, 1962); (b) sloping liner of zero permeability (McBean et al., 1982); sloping liner of permeability K_2 overlain by a landfill of permeability K_1 (Wong, 1977).

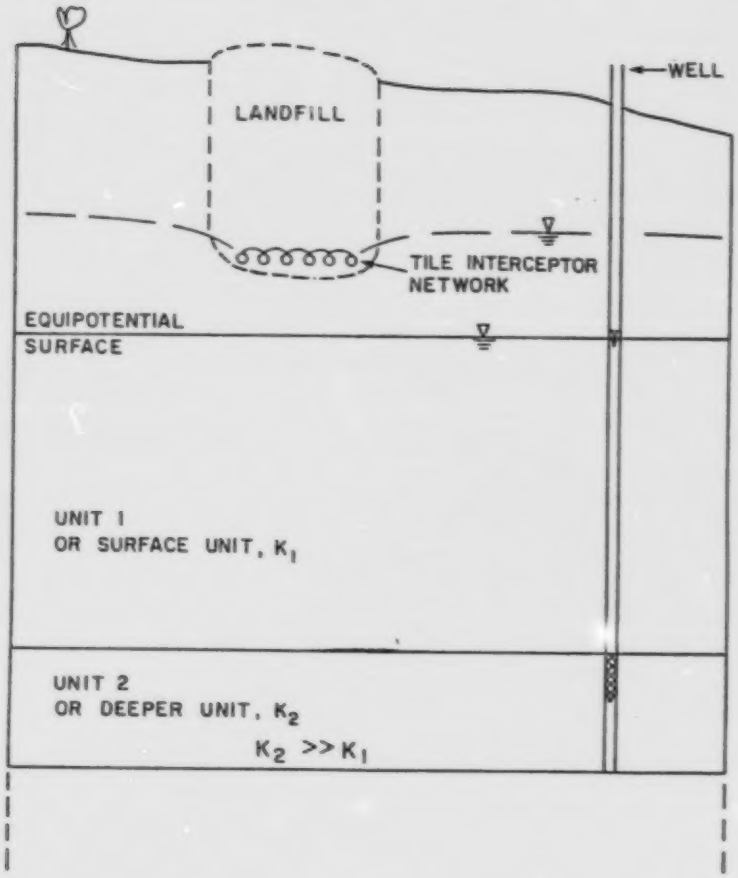

WELL
LANDFILL
TILE INTERCEPTOR NETWORK
EQUIPOTENTIAL SURFACE
UNIT 1
OR SURFACE UNIT, K_1
UNIT 2
OR DEEPER UNIT, K_2
$K_2 >> K_1$

Figure 2. Schematic view of a landfill site.

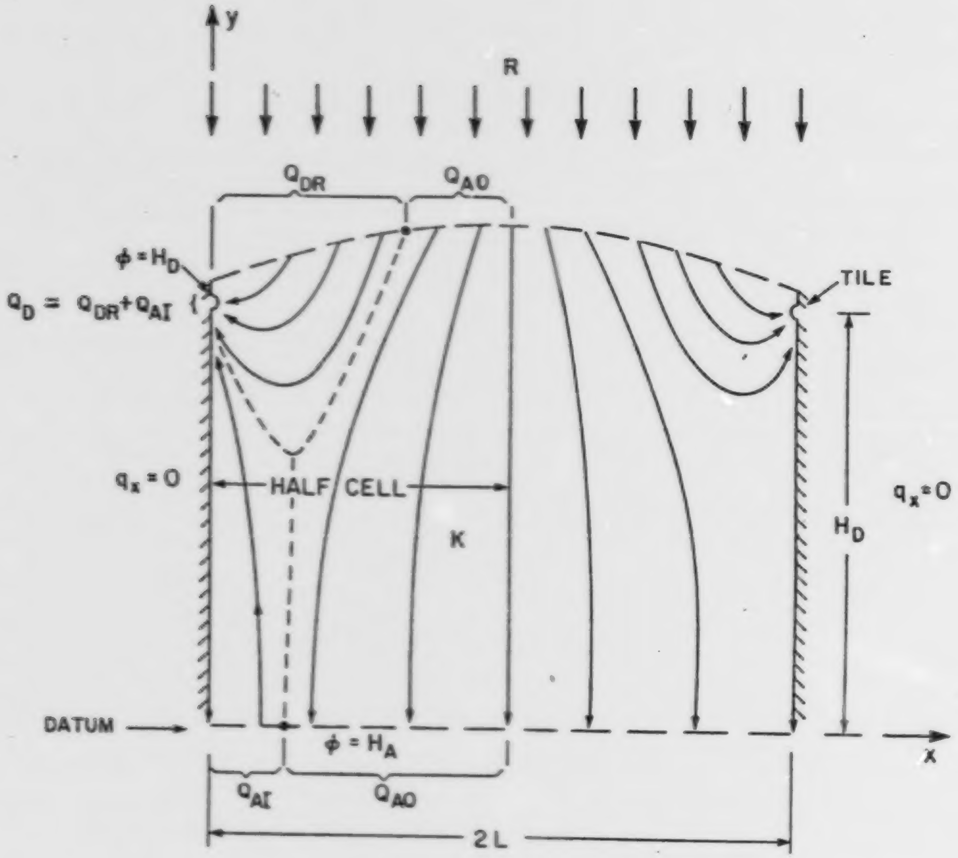

y
R
Q_{DR}
Q_{AO}
$\phi = H_D$
$Q_D = Q_{DR} + Q_{AI}$
TILE
$q_x = 0$
HALF CELL
K
$q_x = 0$
H_D
DATUM
$\phi = H_A$
x
Q_{AI}
Q_{AO}
2L

Figure 3. Drainage cell with boundary conditions and symbols.

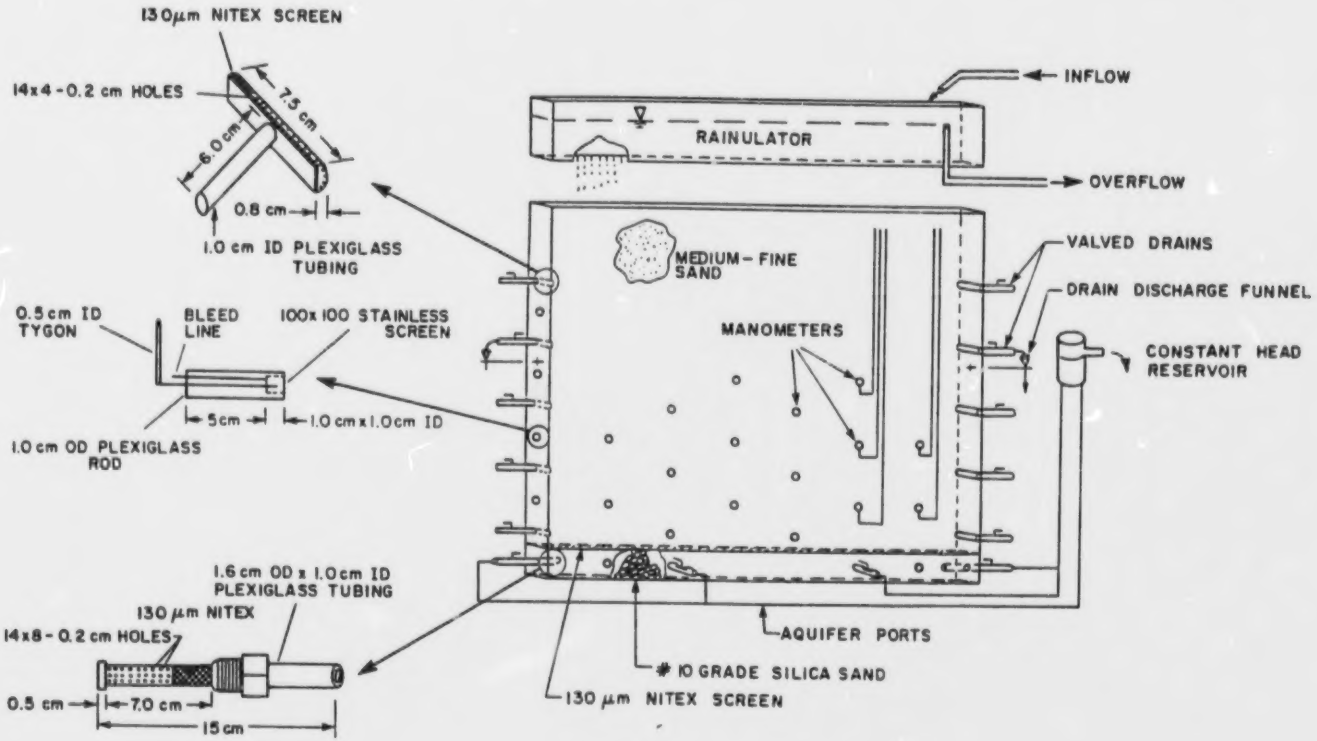

130μm NITEX SCREEN
14x4 - 0.2 cm HOLES
7.5 cm
6.0 cm
0.8 cm
1.0 cm ID PLEXIGLASS TUBING
0.5cm ID TYGON
BLEED LINE
100x100 STAINLESS SCREEN
5cm
1.0 cm x 1.0cm ID
1.0 cm OD PLEXIGLASS ROD
1.6 cm OD x 1.0cm ID PLEXIGLASS TUBING
130 μm NITEX
14x8 - 0.2 cm HOLES
0.5 cm
7.0 cm
15 cm
INFLOW
RAINULATOR
OVERFLOW
MEDIUM - FINE SAND
VALVED DRAINS
DRAIN DISCHARGE FUNNEL
CONSTANT HEAD RESERVOIR
MANOMETERS
AQUIFER PORTS
# 10 GRADE SILICA SAND
130 μm NITEX SCREEN

Figure 4. Experimental apparatus. The bottom layer of the box was packed with # 10 grade silica sand with a saturated hydraulic conductivity of 2.5 X 10^{-1} cm/s. The top layer was made of Chalk River medium fine-grained sand with a saturated hydraulic conductivity of 4.2 X 10^{-3} cm/s.

VARIABLE	*DESCRIPTION*	*UNITS*
Qr	Recharge of leachate	L^3/T
Qao	Discharge of fluid leaving system through bottom	L^3/T
Qai	Recharge due to fluid entering system through bottom	L^3/T
Qa	Resulting discharge at the bottom of the system (Qa=Qai+Qao)	L^3/T
Qd	Discharge of fluid leaving system through drain	L^3/T
Qdr	Discharge of leachate collected by the drain	L^3/T
Ha	Hydraulic head along the bottom of system.	L
Hd	Hydraulic head at drain.	L
L	Half spacing between drains.	L
R	Recharge flux.	L/T
K	Saturated hydraulic conductivity.	L/T
Qa/Qr	Response factor.	-
R/K	Hydraulic condition factor.	-
Ha/Hd	Induced head ratio.	-
Hd/L	Cell geometry factor.	-

Table 1. Description of variables and ratios used in the study.

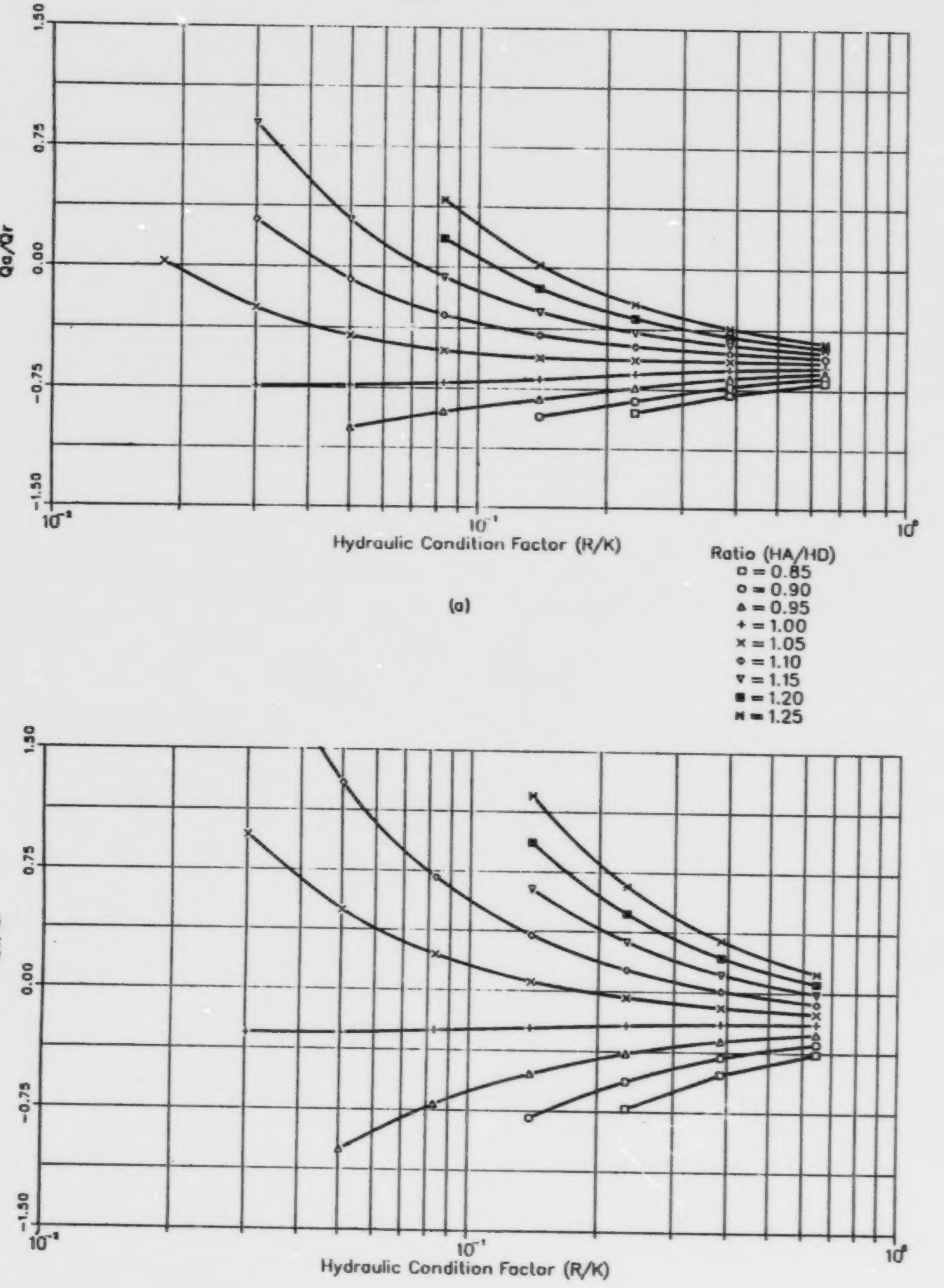


Figure 5. Response curves showing the relation between R/K and the response factor Qa/Qr. (a) Hd/L = 0.75, (b) Hd/L = 4.00. A comparison between the two sets of curves shows that collection is better as the drain spacing decreases.

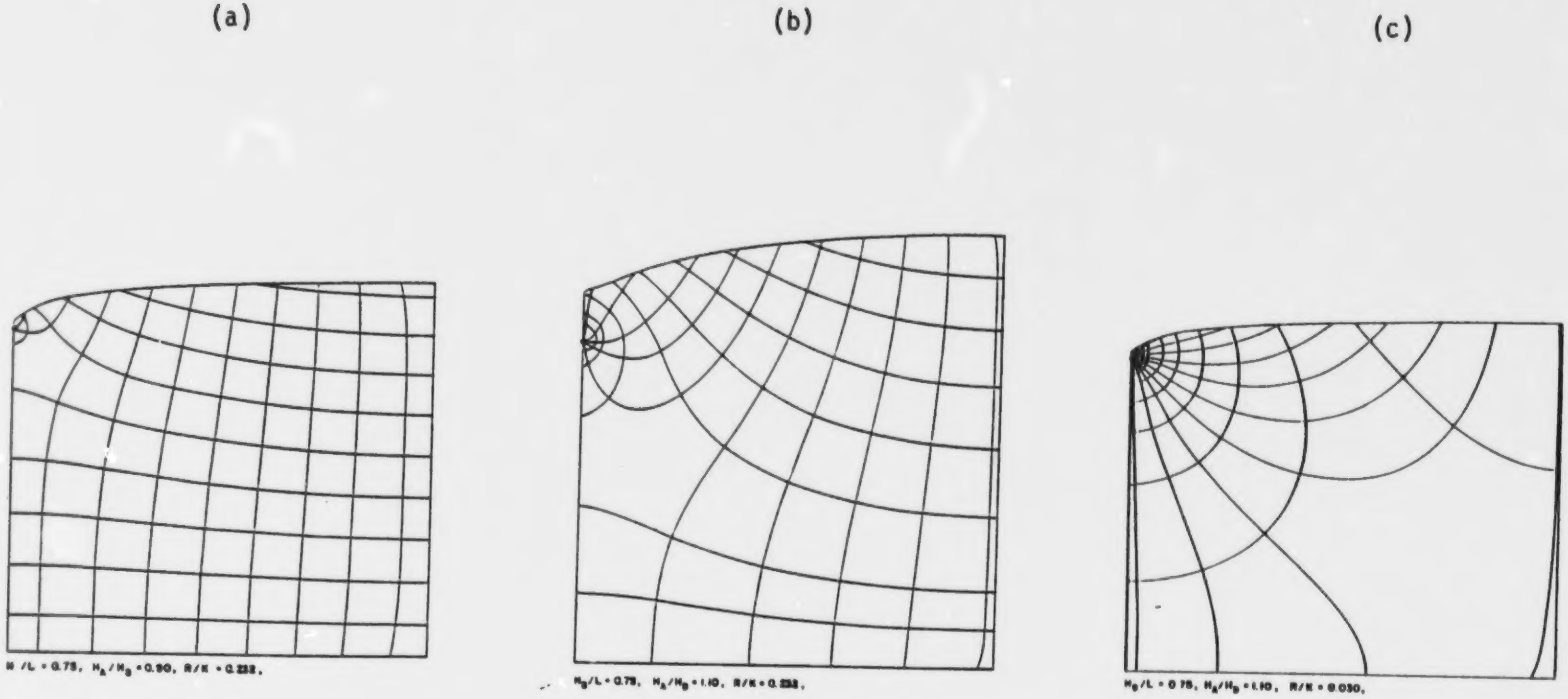

(a)
(b)
(c)
$H/L = 0.75$, $H_A/H_B = 0.90$, $R/K = 0.232$,
$H_B/L = 0.75$, $H_A/H_B = 1.10$, $R/K = 0.232$,
$H_B/L = 0.75$, $H_A/H_B = 1.10$, $R/K = 0.030$,

Figure 6. Flownets illustrating different flow conditions that may occur inside the half cell: (a) most of the leachate bypasses the drain, (b) approximately half of the leachate is collected, (c) all of the leachate is collected and infiltration from the bottom is occuring.

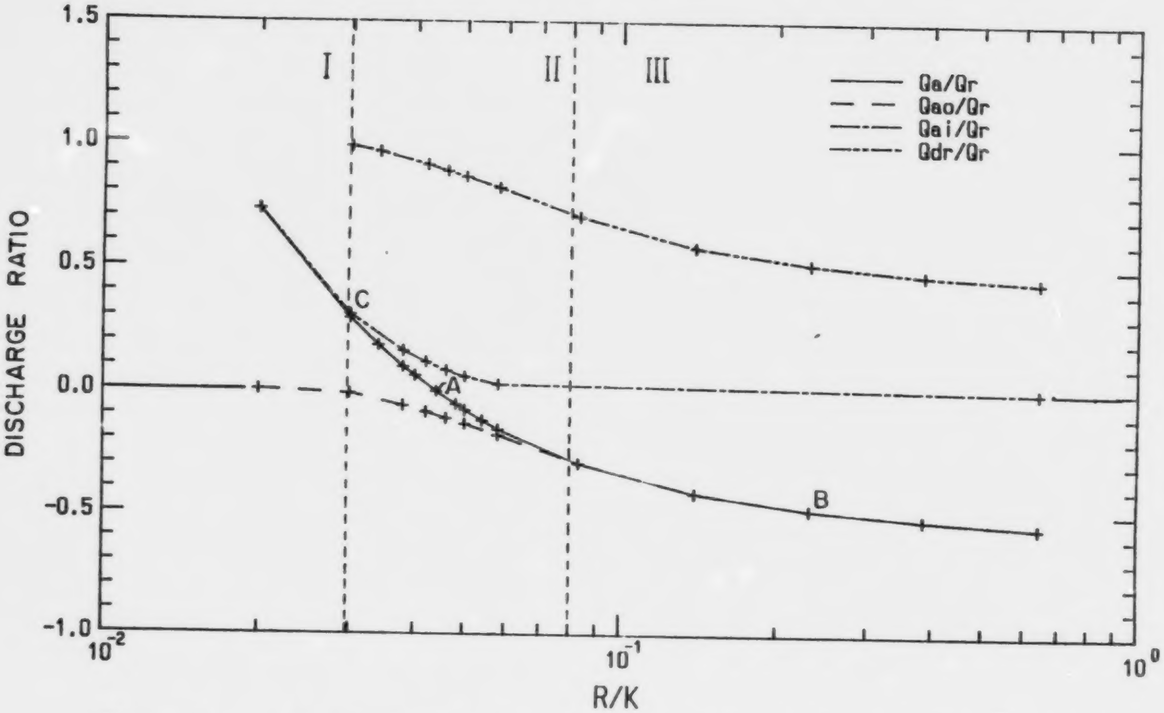
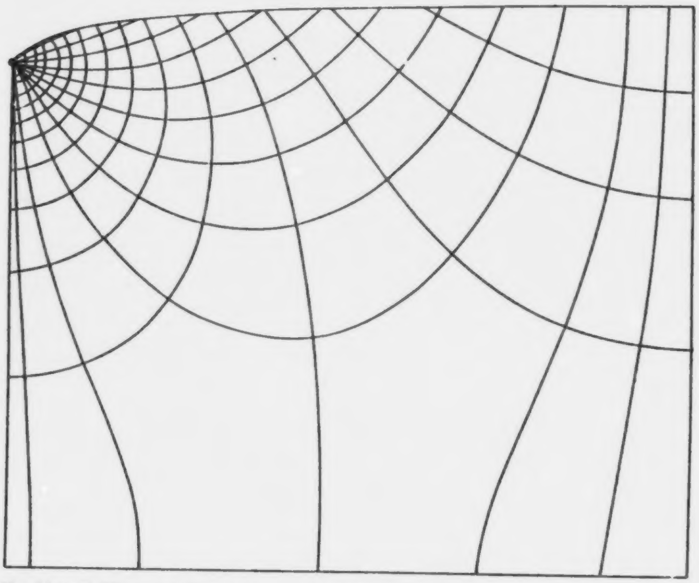


Figure 7. Response curve for conditions Hd/L = 0.75 and Ha/Hd = 1.10 (solid line) plotted along with the values of the other discharge ratios Qao/Qr, Qai/Qr and Qdr/Qr (dashed lines). Points B and C correspond to flownets 6b and 6c.



$H_D/L = 0.75$, $H_A/H_D = 1.10$, $R/K = 0.044$, $Q_A/Q_R = 0$

Figure 8. Flow conditions occuring at point A on figure 7.

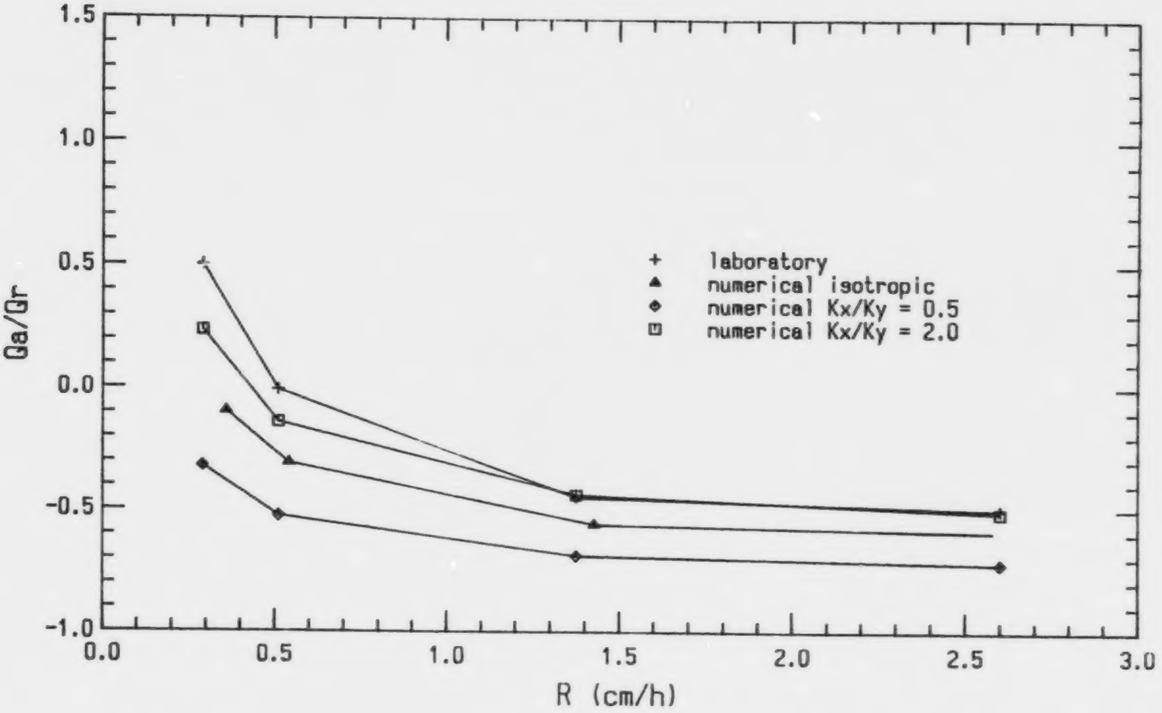


Figure 9. Laboratory and numerical response curves for $Hd/L = 0.64$ and $Ha/Hd = 1.06$. The value of Ky is constant at 4.2×10^{-3} cm/s.

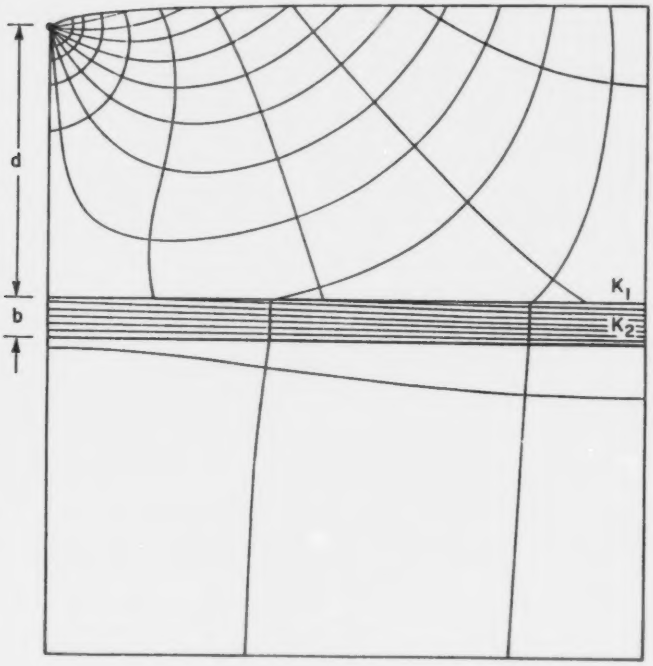


Figure 10. Half cell flow system including a low permeability layer.

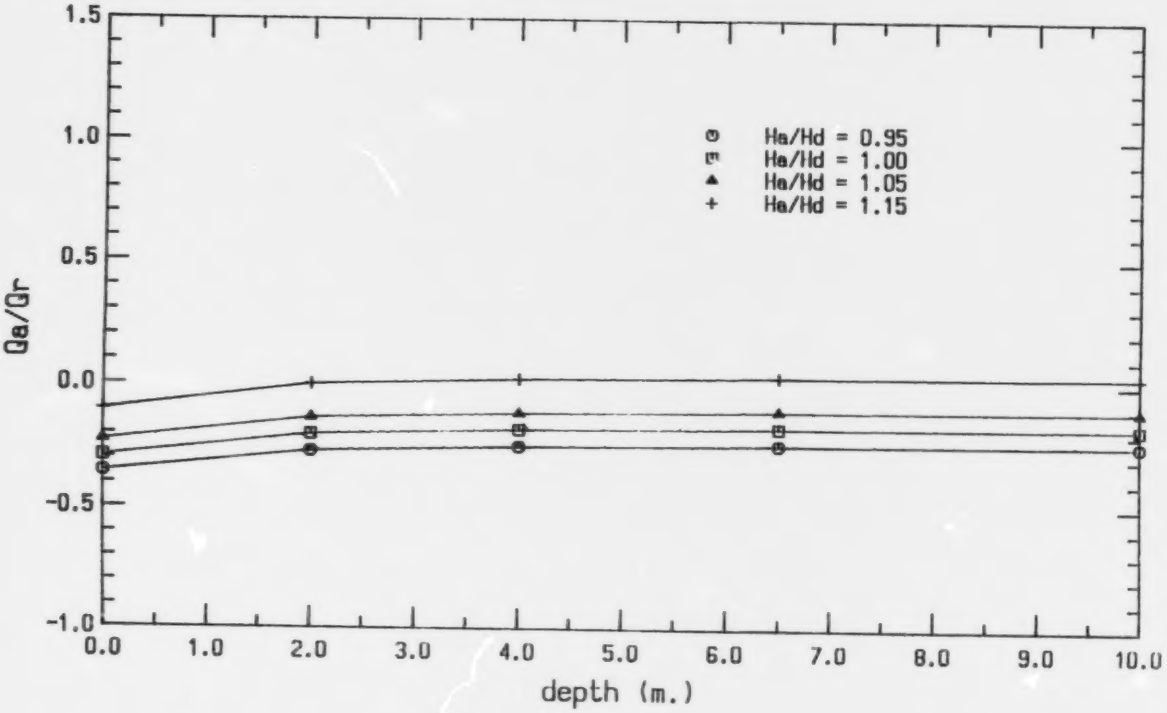


Figure 11. Response of the half cell system versus the depth of the low permeability layer for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), $K_1/K_2 = 100.0$ ($K_1 = 1.2 \times 10^{-3}$ cm/s, $K_2 = 1.2 \times 10^{-5}$ cm/s), $R = 9.6 \times 10^{-5}$ cm/s., b = 1m.

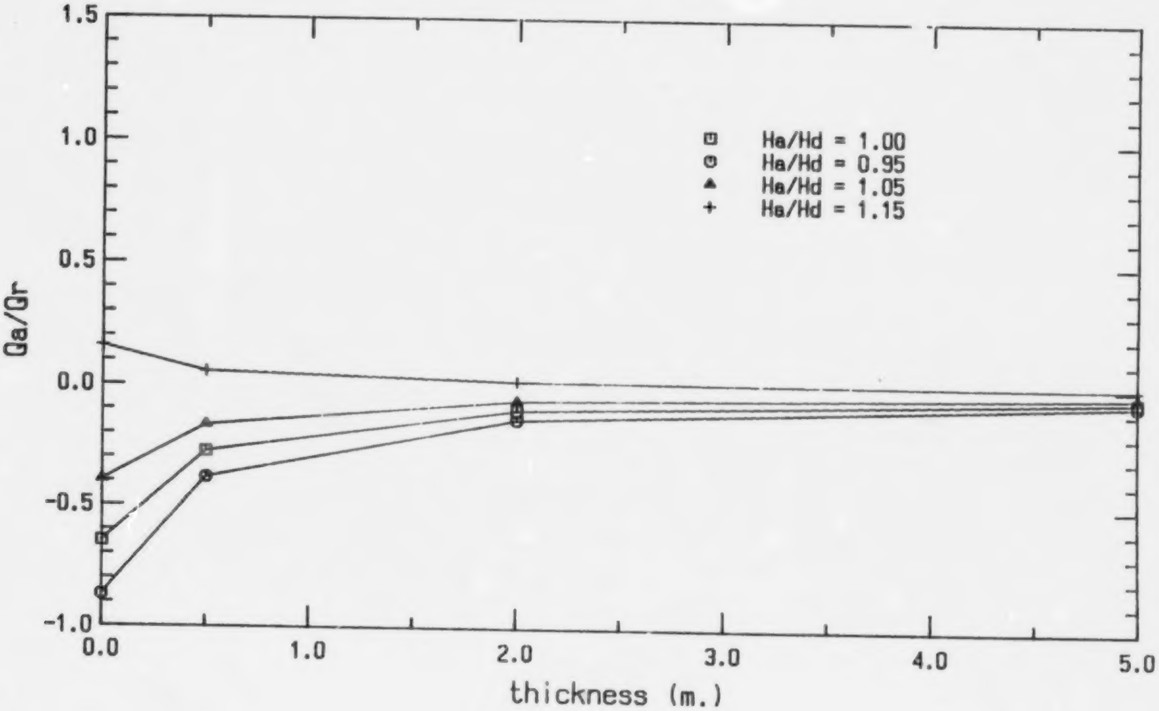


Figure 12. Response of the half cell system versus the thickness of the low permeability layer for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), K_1/K_2 = 100.0 ($K_1 = 1.2 \times 10^{-3}$ cm/s, $K_2 = 1.2 \times 10^{-5}$ cm/s), R = 9.6×10^{-5} cm/s., d = 6.5 m.

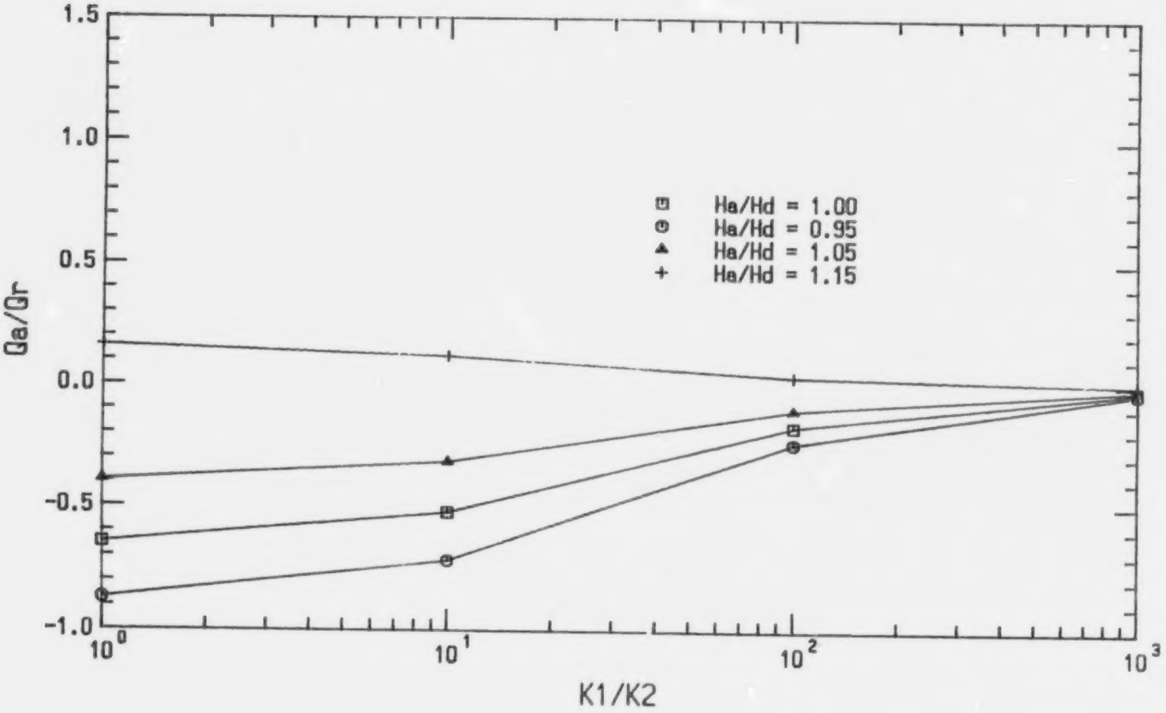


Figure 13. Response of the half cell system versus the hydraulic conductivity contrast between the low permeability layer and the rest of the cell for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), $K_1 = 1.2 \times 10^{-3}$ cm/s, $R = 9.6 \times 10^{-5}$ cm/s., d = 6.5 m., b = 1.0 m.

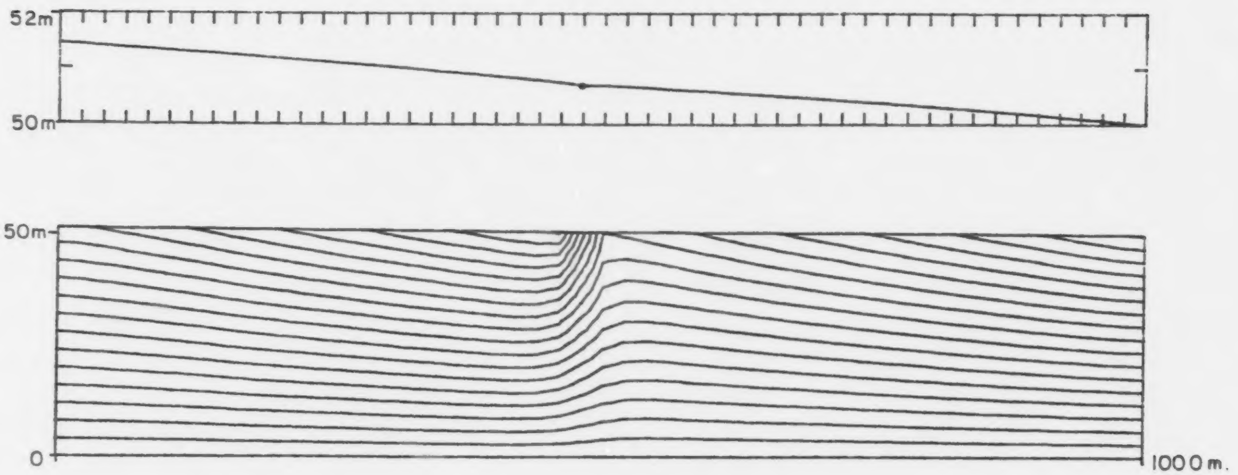

52m
50m
50m
0
1000 m.

Figure 14. Flowlines describing drainage in a horizontal flow system.

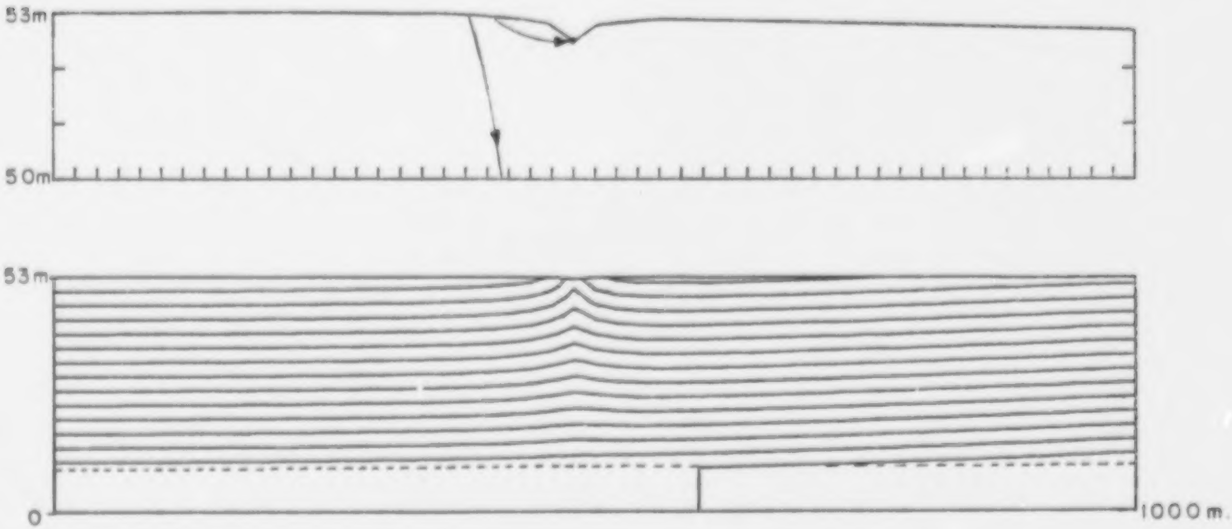


Figure 15. Equipotential lines for drainage in a vertical flow system.

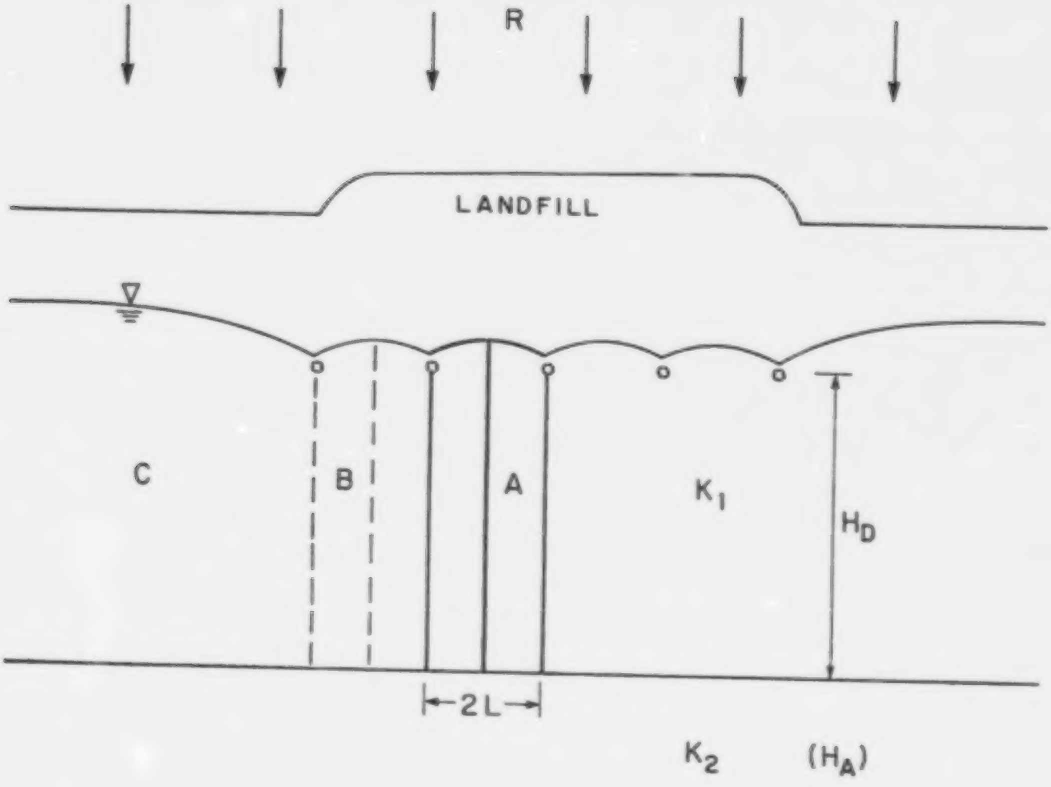

R
LANDFILL
C
B
A
K_1
H_D
2L
K_2
(H_A)

Figure 16. Groundwater flow zones under a landfill located in a low permeability hydrogeological unit.

AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO

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Abstract

Recent research has indicated that the rate of degradation of organic compounds in ground water is dependent on the existing redox conditions. A detailed redox survey was carried out at the Gloucester Landfill site, Gloucester, Ontario, in 1985, to establish the redox conditions within a contaminant plume containing volatile organics. The redox conditions were characterised three ways: (1) EH measurements were made using a platinum electrode connected to a flow cell. PH and temperature probes were also connected to the flow cell so that all three field measurements could be recorded at the same time; (2) dissolved oxygen measurements were carried out with a second, independent, flow cell; (3) field and laboratory measurements of sulphate and sulphide concentrations in the ground water were carried out. These values were used to calculate a Nernstian "pe" for each sampling location. A concurrent study into the distribution of volatile organics on the site provided the contaminant data.

Redox conditions at the Gloucester site cannot be well defined by any single method. Measured Eh values were found to be imprecise and inaccurate, although general trends were evident in the data. Calculated Eh values could only be determined over a narrow range due to the analytical detection limits of the sulphide and sulphate analyses. Dissolved oxygen measurements do not reflect concentrations of other oxidized species which may affect the Eh.

Two transformations which may be occurring in the plume are trichloroethane to 1,1 dichloroethane, and toluene to carbon dioxide or methane. These processes appear to be proceeding very slowly.

Introduction

The Gloucester Landfill overlies an unconsolidated sedimentary sequence of interstratified sands, silts and gravels interpreted as littoral and sublittoral esker-fan deposits of the Champlain Sea (Rust and Romanelli, 1975). This sequence comprises two aquifer systems. A confined aquifer, approximately 20 m thick, overlying bedrock, is overlain by a silty clayey aquitard, 2-3 m thick, which is , in turn, overlain by the water table aquifer (about 6 m thick).

The landfill is located 2 km south of the Ottawa International Airport on the eastern flank of a northwest-southeast trending sand and gravel ridge which acts as a local ground water divide (Figure 1).

A detailed redox survey of the conditions within and around a contaminant plume in the unconfined aquifer at the Gloucester Landfill site was completed during the summer of 1985. Simultaneously, a separate study of the extent and distribution of volatile organic compounds within this leachate plume was also undertaken.

The purpose of this paper is to present the combined results of these studies in an effort to show the relationships between the redox conditions and the organic contaminant distribution within the leachate plume.

Site Hydrogeology

Recharge conditions prevail throughout the landfill west of the C.P.R. tracks (Gartner Lee, 1978). Vertical gradients between the shallow and confined aquifers gradually decrease eastward in the study area, reflecting the discharge conditions which prevail at the eastern end of the site.

The ground water flow direction was determined to be toward the east on the basis of water table elevation data collected using an electric sonde.

The hydraulic conductivity of the aquifer material was determined by Hvorslev´s method for single piezometer slug tests (Freeze & Cherry, 1979). Results indicate that K ranges between 5.9×10^{-6} and 5.1×10^{-5} m/s.

Estimates of the ground water velocity range from <1 cm/day to 14 cm/day on the basis of point dilution measurements and hydraulic gradients.

Field Methods

Fifteen piezometers and twenty-two multilevel samplers were monitored at the northeast plume site (Figure 2). Measurements of pH, Eh and temperature were conducted in an air-tight flow cell using a mercury thermometer and combination pH and platinum electrodes (from Orion Research Inc.) connected to a battery powered Metrohm pH/mV/T meter. The flow cell was flushed at approximately 100 ml/min for a minimum of 10 minutes with the sample prior to taking meter readings. Between each sample measurement the pH and redox electrodes were calibrated; the pH electrode in buffer solutions of pH 4, 7 and 10, and the redox electrode in a poised solution of ferrous ammonium sulphate, ferric ammonium sulphate and sulfuric acid with a redox potential of +475 mV (Light, 1972).

Dissolved oxygen concentrations and temperature were measured using an Orbisphere Dissolved Oxygen Meter (model #2713). Calibration was carried out at the beginning of each day by zeroing the meter reading with the sensor immersed in a 10% by weight sodium sulfite solution. The sensor was stored in this anaerobic solution when not in use.

Sulphide measurements were made in the field using a portable HACH DREL 2 Spectrophotometer with range expander. The HACH Methylene Blue method was used for the determination of total sulphide.

The spectrophotometer was calibrated at each multilevel sampling location using daily prepared fresh sulphide standards. These precautions ensured that: (1) fluctuations in the power source which caused changes in the calibration curve were compensated for; and (2) the calibration curves were not affected by the rapid decay of sulphide standards.

Samples for sulphate analysis were collected in glass vials immediately following the sulphide analyses and transported to the National Hydrology Research Institute laboratory at the end of the day. All samples were refrigerated at 8°C until analysed.

Samples for the analysis of volatile organic compounds were collected using a peristaltic pump and stored in polypropylene syringes. The collection system, developed by Farrington Lockwood Co. Ltd. (1983), permits the collection and analysis of the samples to occur without ever exposing them to the atmosphere. All parts of the sampling equipment that come into direct contact with the water being sampled were transported to and from the field in sealed plastic bags inside a tightly sealed cooler; this measure prevented exposure to, and contamination from, gasoline fumes.

Analytical Methods

Sulphate analyses were performed on the HACH DREL 2 Spectrophotometer using the HACH turbidimetric method. All sulphate samples were analysed within 10 days of sampling.

Analyses for weak organic acids were carried out using a Dionex System 12 Analyser in the Ion Chromatography Exclusion Mode (I.C.E.). Acetate and chloride analyses were also performed by standard Ion Chromatography.

Volatile organic compounds were analysed using a Spectra-physics Model 7100 Gas Chromatograph equipped with an Envirochem Unacon 810 purge and trap unit. Samples (15 mLs) were purged 12 minutes with high purity helium gas. Separation of the compounds was achieved with a 0.25 mm diameter wall coated open tubular capillary column. The system was equipped with both F.I.D. and Hall detectors.

Results

Nernstian Eh values were calculated on the basis of the $SO_4^{=}/HS^-$ couple using the following equations from Stumm and Morgan, (1981).

$$pE = 4.25 - 1.125\ pH + 0.125\ pSO_4^{=} - 0.125\ pHS- \qquad (1)$$

$$Eh = 0.059\ pE \qquad (2)$$

In order to obtain representative values of HS^- from total sulphide measurements for the above calculation, it was necessary to assume equilibrium conditions and that;

$$\text{total sulphide} = H2S + HS^- + S^{2-} \qquad (3)$$

The range of Eh values determined using equations (1) and (2) is only -150 mv to -300 mv. In general, the lowest values correspond to measurements taken from the bottom of the unconfined aquifer. However, in a few locations low Eh´s were determined in near surface ground water (99PM, 107M, 108M). In these instances it is thought that local conditions, such as those produced by buried vegetation, are responsible for the sulfur content of the water, and hence the apparently low Eh.

Eh values, measured using the platinum electrode, range from about 0 mv to 550 mv. In general, the highest values correspond to shallow locations (ie. at depths of about 2 m). There is some suggestion in the data that the shallow ground water at the site is increasingly oxidizing toward the east. In the deeper ground water, the lowest Eh values occur in the areas of greatest organic contamination.

Dissolved oxygen concentrations range between 4 ppm and <0.1 ppm (100 ppb). The highest concentrations were measured in the very shallow regions of the aquifer. The concentrations dropped off rapidly to values of less than 150 ppb for most of the aquifer thickness.

Significant noise was encountered when oxygen concentrations fell below 100 ppb (+/- 15%). Oxygen, entering the flow cell through the polyethylene and silicone tubing of the monitor and the pump, may account for this background noise (Orbisphere Laboratories).

Volatile Organic Contamination

Twenty volatile organic compounds have been identified in the ground water at the northeast plume site by G.C./M.S. Of these, 1,2 dichloroethane (12DCEA), benzene, trichloroethylene (TCEY), toluene, and chlorobenzene (ClBENZ) have been studied quantitatively. Tetrahydrofuran (THF) and diethyl ether (DEE) have been tentatively identified by G.C. and also studied quantitatively, but their presence has not been confirmed by M.S. A detailed description of the distributions of all these compounds can be found elsewhere (Devlin and Gorman, in press). For the purposes of this discussion, the distributions of benzene and toluene are described and are typical of the distributions of the other volatile organic contaminants (Figures 2 and 3).

The source of the organic contamination seems to be located west of the study site. The plume appears to be migrating along a very narrow path between 99M and 100PM (25 m wide) and extends east beyond 118M. However, the lack of lateral control east of 112M restricts a firm definition of the plume width to the western and central portions of the study area. Both toluene and benzene show two concentration maxima: a well defined maximum between 109M and 113M, and a poorly defined maximum beginning near 118M and extending east. In section, the contaminants appear to be following two flow paths: in the western portion of the study area, low levels of toluene (not shown in Figure 3) occur at a depth of about 4-5 m while the remaining chemicals are most concentrated at depths of 6-7 m. East of 109M, the plume appears to be migrating at about 5 m depth. This pattern continues until 115M and 117M where the concentration maxima are once again at 6 - 7 m depth.

DISCUSSION

The three methods used to investigate the redox conditions at the study site are, ideally, examining different manifestations of the same process. Thus, in the ideal case one might expect perfect correlations between:

(1) Eh (measured) and Eh (calculated).
(2) Eh and dissolved O_2 concentration.

However, when these parameters are plotted against one another the correlations are weak (Figures 4 and 5). This indicates that ideal conditions do not exist at the study site, and in order to interpret the data close attention must be paid to exactly what is being measured by each method.

Considerable research has been carried out to determine the relationship between Eh values measured using a platinum electrode and those predicted by thermodynamics (Baas Becking et al., 1960; Garrels and Christ, 1965; Stumm and Morgan, 1981; Jackson and Patterson, 1982). The electrode measures an exchange current produced during the course of oxidation reduction reactions. "Slow" electrodes, where there is a large change in electrode potential required to induce a measurable exchange current, and "mixed" potentials, in which several redox processes may be involved in the apparent "equilibrium" potential, have been cited as causes of imprecise and inaccurate Eh measurements, respectively (Stumm and Morgan, 1981).

Jackson and Patterson (1982) found that field measurements of Eh using a platinum electrode were consistently higher than Eh values determined indirectly using analytical information ($H_2S/SO_4^=$). A similar trend has been observed in the data from the Gloucester site. There are two possible causes for the observed discrepancy in values: (1) the measured potentials are actually "mixed" potentials, and do not accurately reflect the equilibrium Eh values; (2) the assumption of equilibrium, which is implicit in the indirect evaluation of Eh, is unjustified. The former cause was considered to be the most likely one by Jackson and Patterson (1982). It should be noted that although the measured Eh values may be inaccurate in a quantitative sense, they may still be useful in a qualitative analysis. For example, oxidizing solutions will exhibit higher Eh´s than reducing solutions.

Although the indirect method of determining Eh values may provide more accurate data, there are limitations to the procedure. To begin with, as noted above, the system under study must be in equilibrium. Secondly, both members of the couple must be present at concentrations which are measurable. This constraint severely limits the range of Eh values which can be determined using any one couple (Cherry et al., 1979). For example, when the $H_2S/SO_4^=$ couple is used to determine Eh values, a 10,000 fold change in the relative concentrations of the two members only corresponds to a 30 mV difference in the calculated Eh´s (Table 1). So, at a site where there is a wide variation in Eh conditions, a single redox couple will be insufficient to define all those conditions.

Table 1: Calculated Eh values for various concentrations of H_2S and $SO_4^=$.

Concentrations				Eh (calc.)
H_2S		$SO_4^=$		(mv)
ug/L	moles/L	mg/L	moles/L	
5	1.47×10^{-7}	200	2.08×10^{-3}	-183
50	1.47×10^{-6}	20	2.08×10^{-4}	-198
500	1.47×10^{-5}	2	2.08×10^{-5}	-212

calculations were performed assuming a pH of 7.

Water saturated with air has an oxygen content of about 8 ppm at 20°C. But at what concentrations of oxygen are waters considered to be "anoxic"? Stumm and Morgan (1981) have used the term "anoxic" to describe systems in which the supply of dissolved oxygen is depleted to the extent that the primary oxidizing agent is nitrate (or another lesser oxidized species). Such a system could have a theoretical Eh of more than 300 mv (Stumm and Morgan, 1981, pp. 459). Thus, it is possible for a solution low in dissolved oxygen to exhibit a relatively high Eh. This seems to be the case in some locations at the Gloucester site (Figure 5).

It can be seen from the above that dissolved oxygen measurements cannot, by themselves, define the redox environment of a site. However, oxygen is involved in many biologically mediated reactions and a direct measurement of its availability to organisms can be invaluable in predicting the transformation products of contaminants in ground water.

The data which were collected using the three methods have been combined to produce a cross-sectional view of the redox zones within the northeast plume (Figure 6). The map was prepared in two steps: Firstly, an oxygen availability index was calculated based on the $H_2S/SO_4^=$ equilibrium,

$$H_2S_{(aq)} + 2O_{2\,(aq)} = SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \quad K = 1.35 \qquad (4)$$

(K calculated using thermodynamic data from Stumm and Morgan, 1981)

Analytically determined values for pH, sulphate concentration and total sulphide concentration at each monitoring location were inserted into equation (5) to derive a theoretical equilibrium dissolved oxygen concentration.

$$\text{ppb } O_2 = 32 \times 10^6 \sqrt{\frac{(10)^{-2pH}\ (\text{ppm } SO_4^= /96000)}{1.35\ (\text{ppb } H_2S/34 \times 10^6)}} \qquad (5)$$

where,

ppb O_2 = dissolved oxygen concentration in ppb
ppm $SO_4^=$ = sulphate concentration in ppm
ppb H_2S = total sulphide concentration in ppb

The oxygen availability index is defined as a ratio between the theoretical dissolved oxygen concentration and the measured concentration (equation 6).

$$\text{OAI} = \text{ppb } O_2 \text{ (measured)/ ppb } O_2 \text{ (theoretical)} \qquad (6)$$

An index value significantly greater than unity indicates a surplus of available oxygen, while a value less than unity indicates an oxygen depletion. Both these cases also suggest a disequilibrium in the $H_2S/SO_4^=$ redox couple. Values near unity indicate there is equilibrium between the oxygen and sulfur species. In this case, O_2 may or may not be available to react with organic material, depending on the concentrations of other oxidized species.

In the second step of the cross-section preparation, the index values were matched to their corresponding Eh (measured, Pt electrode) values and three zones were defined:

(1) An oxygenated zone in which the OAI>10 and Eh (meas.) is >100 mv.

(2) A transition zone in which 1<OAI<10 or Eh (meas.) is <100 mv or both conditions exist.

(3) A reducing zone in which OAI<1 and Eh (meas.)<100 mv.

The cross-section (Figure 6) shows that the most reducing zones are located at the west side of the study site, near the former disposal trenches, and in the central portion of the site. The transitional zone stretches across the whole site, but appears to be tapering off in the direction of the front of the plume.

Volatile Organics

The relationship between the redox environment and the contamination at the Gloucester Site is clearly evident in Figures 7 and 8. The highest levels of contamination exist in relatively reducing environments. This is true for both aromatic and polyhalogenated contaminants.

The relationship between Eh and chloride is notably less pronounced than that between Eh and the organics (Figure 9). This indicates that the trend evident in Figures 7 and 8 is not merely a function of the flow path of the plume i.e. not all contaminants occur exclusively within the reducing environment of the plume.

There are two explanations for the observed trend:

(1) The organic contaminants in the oxidizing zones of the aquifer have been transformed and are no longer detectable while those in the reducing zones persist due to slow reaction rates. By this reasoning it is the redox environment which determines the apparent distribution of the organics.

(2) The dissolved oxygen (and other oxidized species) is depleted in the zones of severe organic contamination by the oxidation of the contaminants. By this reasoning it is the presence of organics which determines the redox zonation within the aquifer.

Both of the above mechanisms are probably at work at the Gloucester site. Previous research carried out at landfills has indicated that reducing conditions are often encountered in the immediate vicinity of the buried refuse (Baedecker and Back, 1979(a); Nicholson et al., 1982; Hoeks and Borst, 1981). Figure 6 shows that there is a strongly reducing zone located at the west end of the study site near the original disposal trenches. It is possible that this zone was already established when the volatile organics were disposed.

There is also evidence for the second mechanism. According to Figure 6, there is a second reducing zone located at a depth of about 3m at monitor 112M. This zone corresponds in position with the maximum concentrations of benzene and toluene (Figures 2 and 3). Wilson et al. (1986) showed that these compounds can be anaerobically transformed to CO_2. Such a process would be expected to deplete the concentrations of oxidized species, resulting in a reducing zone.

Transformations

The relationship between the redox environment and the fate of various organic compounds has been the subject of much recent research. Reviews of this work have agreed that there is growing evidence that aromatic compounds are most quickly degraded under oxidizing conditions, while most halogenated aliphatic compounds are degraded only under reducing conditions (Jackson *et al.*, 1985; Mackay and Vogel, 1985; Wilson *et al.*, 1986). At the Gloucester site, the organic contamination is restricted to the transitional and reducing zones of the plume. Therefore, this discussion will focus on the anaerobic transformations which might be taking place.

Volatile Fatty Acids

Farquhar and Rovers (1973) reported that complex organic compounds may be fermented anaerobically yielding soluble organic acids which are subsequently transformed to methane and carbon dioxide.

The only identifiable organic acid at the Gloucester site was acetic acid. This substance was only detectable in the zones of severe organic contamination where reducing conditions prevailed. There, it reached concentrations exceeding 1000 mg/L.

The origin of the acetate is unclear. A number of sources have indicated that acetate can be quickly biotransformed in the subsurface (i.e. on the order of weeks) (Hoeks and Borst, 1981; Roberts *et al.*, 1980). Since the contamination has been estimated to be at least 9 years old at the time of sampling (Devlin and Gorman, in press), the continued presence of high concentrations of acetate may be an indication that biological activity at the site is low, and that most of the acetate present was codisposed with the volatile organic wastes.

Halogenated Aliphatics

According to Mackay and Vogel,(1985) the two major chemical reactions for halogenated aliphatics in aqueous solution are hydrolysis (substitution), which leads to the removal of a halogen atom and the formation of an alcohol, and elimination, which leads to the removal of a halogen atom and the formation of an alkene. In addition to these processes, halogenated aliphatics may undergo biologically-mediated transformations which result in the removal of halogen atoms. Parsons and Lage (1985) reported the transformation of TCEA to DCEA; Wilson *et al.* (1986) reported the transformation of TCEY to 12DCEA and ultimately to vinyl chloride.

A possible result of the transformation process is that compounds are produced which are more mobile than the original wastes. This is particularly true with halogenated aliphatics undergoing dehalogenation reactions. However, previous work has indicated that the differences in contaminant mobility at the northeast plume site are small due to the low organic carbon content of the sediments (Devlin and Gorman, in press). Thus, it would be expected that parent-daughter compounds would be detected together wherever the reactions have begun.

At the study site, three pairs of compounds have been identified which could be related by the transformations described above:

(1)	111TCEA --->	11DCEE	Elimination
(2)	111TCEA --->	11DCEA	Dehalogenation
(3)	TCEY --->	11DCEE	Dehalogenation

The distributions of these compounds through the centre of the contaminant plume have been plotted in Figures 10 and 11. Only the second pair of compounds are present in a distribution which is consistent with a parent-daughter relationship. This transformation appears to be occurring in the reducing zone at monitor 112M.

Aromatics

Among the aromatic compounds detected at the study site, benzene and toluene are the most widely distributed (Figures 2 and 3). Aromatics are most quickly biodegraded in an aerobic environment, however, as mentioned previously, anaerobic degradation to CO_2 has also been shown to occur (Wilson et al., 1986). These processes would be expected to deplete the concentrations of oxidized species, resulting in a locally reducing environment.

The maximum concentrations of toluene and benzene occur between monitors 110M and 113M (centering on 112M) where a strongly reducing zone has been defined. Additional maxima have been found at the eastern edge of the site where Eh measurements and dissolved oxygen concentrations indicate that the conditions are transitional to reducing. The concentrations of sulfur species were below the analytical detection limits in this area, so the OAI values could not be calculated.

Although the locations of the concentration maxima are similar for benzene and toluene, the overall distributions of the contaminants differ. Toluene appears to be less diffuse than benzene. This difference could be the result of the more rapid biodegradation of toluene. Wilson et al. (1986) reported that toluene was the only alkylbenzene which did not require a lag time before being anaerobically degraded (other compounds tested included benzene, ethylbenzene and xylenes). Work performed by Water and Earth Science Associates on a gasoline spill, in Eastern Ontario, has shown that toluene is rapidly attenuated while benzene is detectable over the entire length of the plume.

Conclusions

The redox conditions at the Gloucester Landfill site cannot be well defined by a single method. Eh´s measured with a platinum electrode are useful as a qualitative tool to distinguish oxidizing and reducing zones, however, the measurements may be imprecise, due to "slow" electrode response, and they may be inaccurate due to "mixed" potentials in the ground water.

Eh´s determined from analytical data may accurately reflect the conditions of the ground water, however, it is only possible to calculate values within a narrow Eh range. Beyond this range, the members of the redox couple are not analytically detectable.

Dissolved oxygen measurements provide information about the availability of oxygen but not about the availability of other oxidized species which could influence the solution Eh.

Organic contaminants at the site were found to exist only within the more reducing portions of the aquifer. This is probably due to slow reaction rates within existing reducing zones, and transformations which have depleted the concentrations of oxidized species within the aquifer.

Two possible transformations have been identified in the leachate plume: trichloroethane to 1,1 dichloroethane and toluene to CO_2 or CH_4. Both of these processes are taking place near the most reducing portion of the plume. The high concentrations of acetate detected in this area suggest that any biologically mediated transformations are proceeding very slowly.

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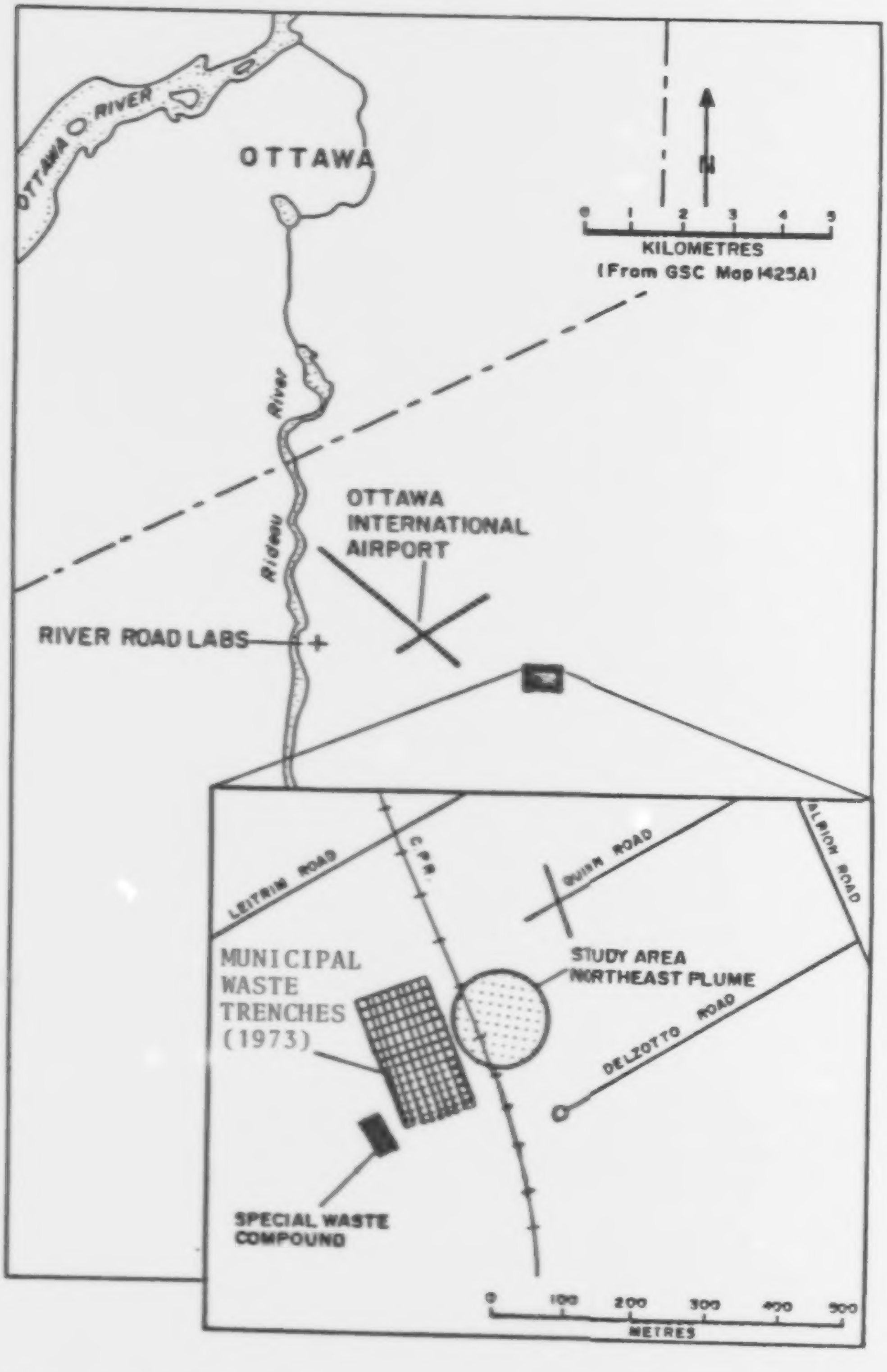

OTTAWA RIVER
OTTAWA
N
0 1 2 3 4 5
KILOMETRES
(From GSC Map 1425A)
Rideau River
OTTAWA INTERNATIONAL AIRPORT
RIVER ROAD LABS
LEITRIM ROAD
C.P.R.
QUINN ROAD
ALBION ROAD
MUNICIPAL WASTE TRENCHES (1973)
STUDY AREA NORTHEAST PLUME
DELZOTTO ROAD
SPECIAL WASTE COMPOUND
0 100 200 300 400 500
METRES

Figure 1: The location of the Gloucester Landfill and the northeast plume site, Gloucester, Ontario.

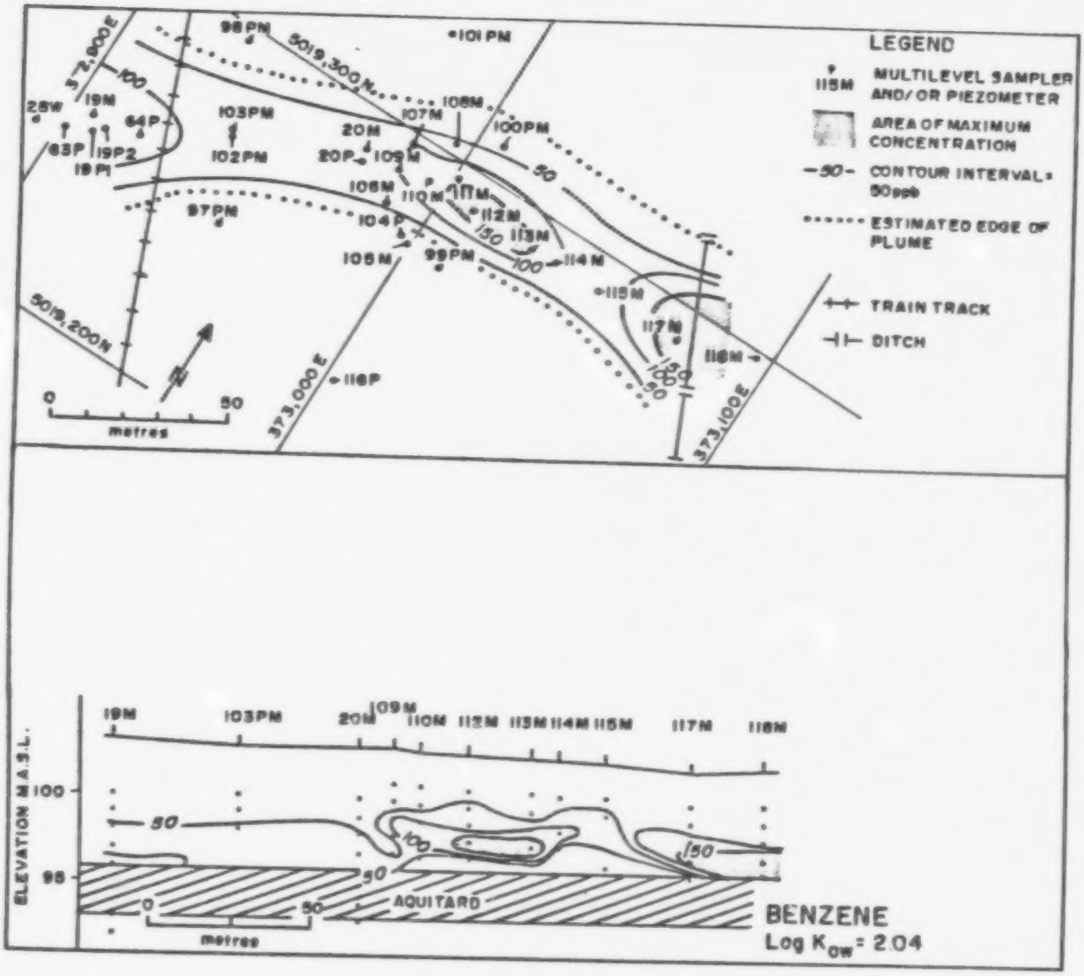

LEGEND
115M MULTILEVEL SAMPLER AND/OR PIEZOMETER
AREA OF MAXIMUM CONCENTRATION
-50- CONTOUR INTERVAL= 50ppb
ESTIMATED EDGE OF PLUME
TRAIN TRACK
DITCH
372,900E
373,000E
373,100E
5019,300N
5019,200N
98PM
101PM
28W
19M
64P
63P
19P2
19P1
103PM
102PM
20M
20P
109M
107M
108M
100PM
106M
110M
111M
112M
113M
114M
104P
105M
99PM
97PM
115M
117M
118M
116P
100
150
50
0
50
metres
19M
103PM
20M
109M
110M
112M
113M
114M
115M
117M
118M
ELEVATION M.A.S.L.
100
95
AQUITARD
BENZENE
Log K_ow = 2.04

Figure 2: The distribution, in plan and section, of benzene at the northeast plume site.

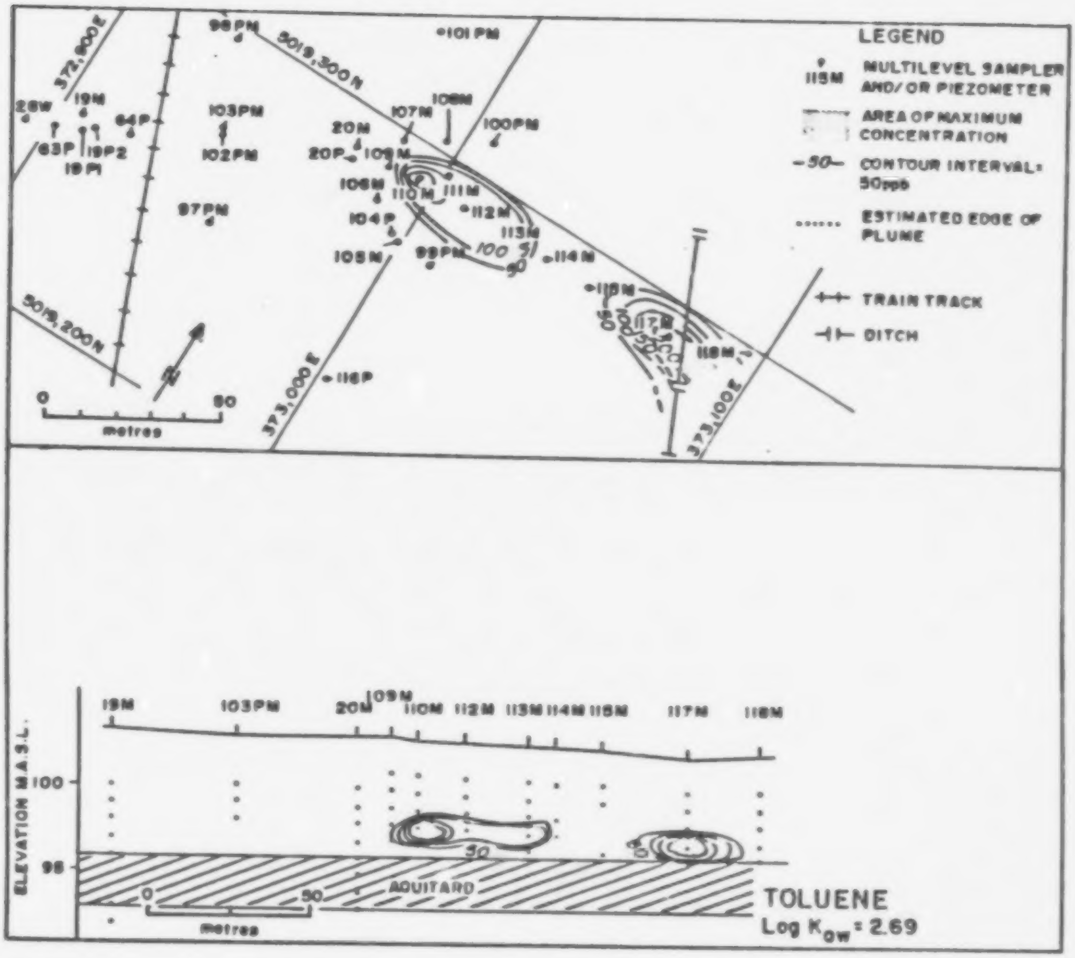

LEGEND
115M MULTILEVEL SAMPLER AND/OR PIEZOMETER
AREA OF MAXIMUM CONCENTRATION
-50- CONTOUR INTERVAL= 50ppb
ESTIMATED EDGE OF PLUME
TRAIN TRACK
DITCH
372,900E
373,000E
373,100E
5019,300N
5019,200N
98PM
101PM
28W
19M
64P
63P
19P2
19P1
103PM
102PM
97PM
20M
20P
107M
108M
109M
100PM
106M
110M
111M
112M
113M
104P
105M
99PM
114M
115M
117M
118M
116P
100
51
50
N
0
50
metres
ELEVATION M.A.S.L.
100
98
AQUITARD
TOLUENE
Log K_{ow} = 2.69

Figure 3: The distribution, in plan and section, of toluene at the northeast plume site.

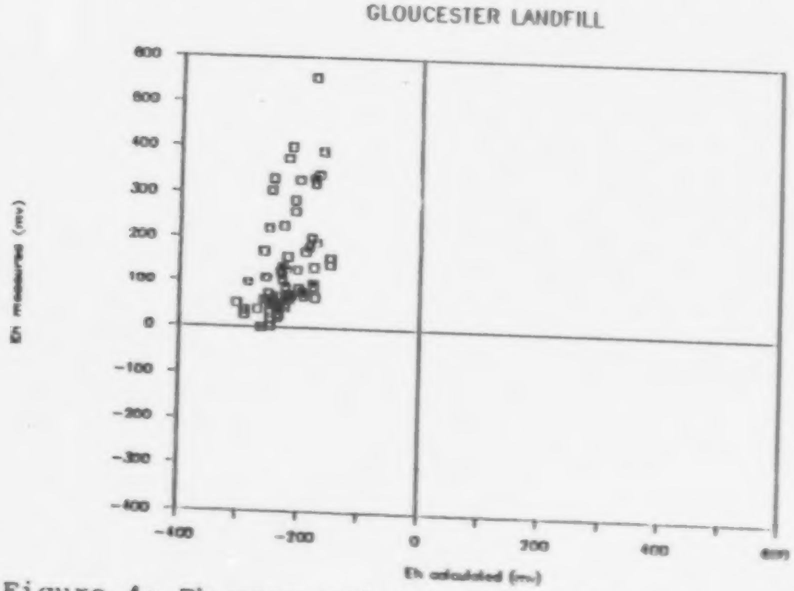


Figure 4: Eh measured (Pt electrode) vs. Eh calculated ($H_2S/SO_4^=$).

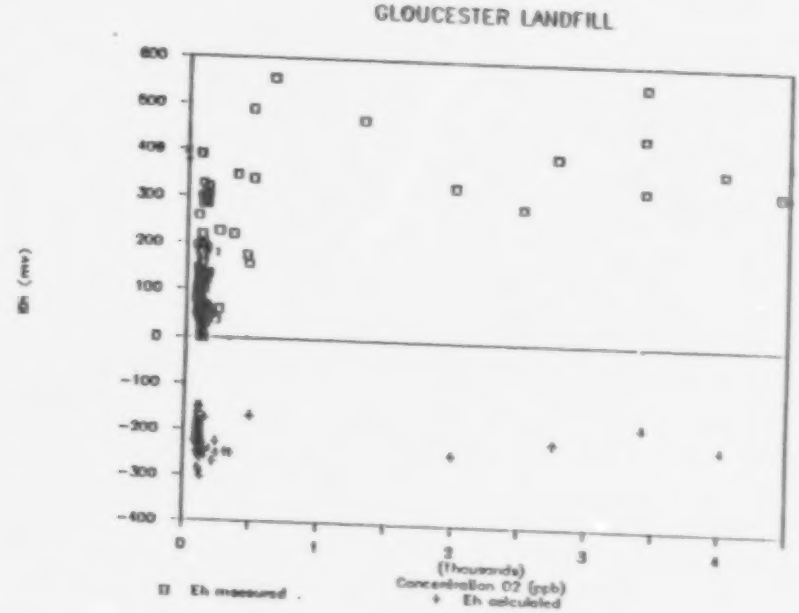


Figure 5: Eh measured (Pt electrode) vs. dissolved oxygen concentration.

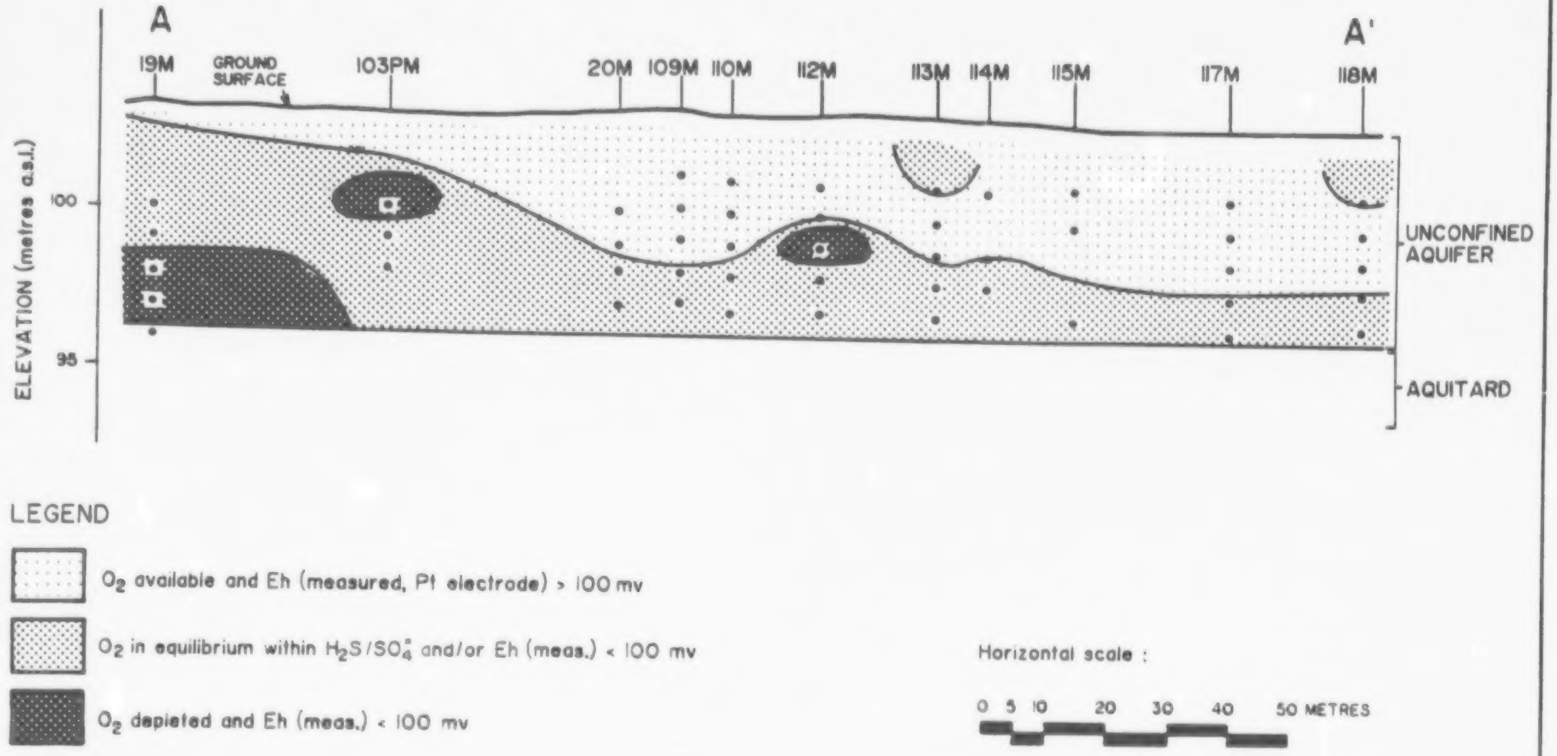

A
A'
19M
GROUND SURFACE
103PM
20M
109M
110M
112M
113M
114M
115M
117M
118M
ELEVATION (metres a.s.l.)
100
95
UNCONFINED AQUIFER
AQUITARD
LEGEND
O_2 available and Eh (measured, Pt electrode) > 100 mv
O_2 in equilibrium within $H_2S/SO_4^{=}$ and/or Eh (meas.) < 100 mv
O_2 depleted and Eh (meas.) < 100 mv
Horizontal scale :
0 5 10 20 30 40 50 METRES

FIGURE 6

REDOX ZONES WITHIN THE NORTHEAST PLUME

WATER AND EARTH SCIENCE ASSOCIATES LTD.

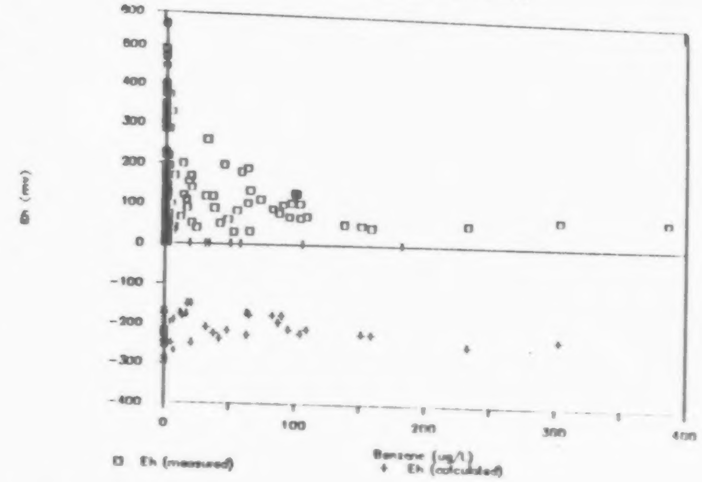


Figure 7: Eh vs. concentration benzene.

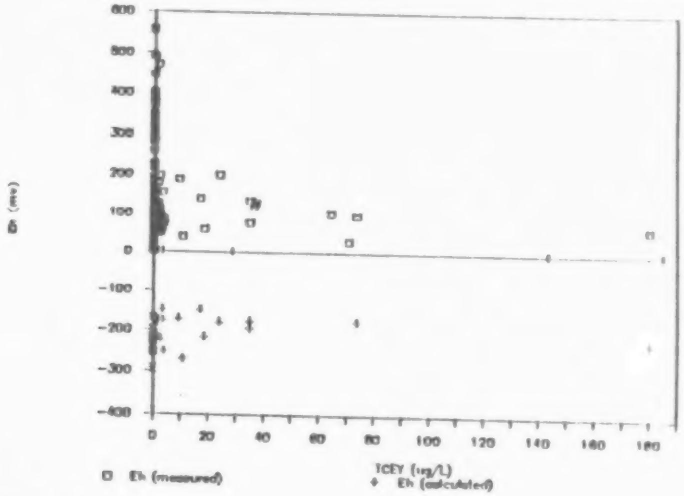


Figure 8: Eh vs. concentration trichloroethene

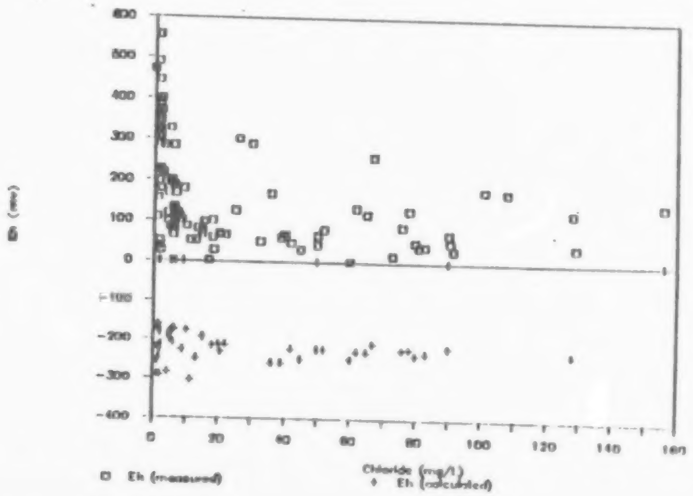
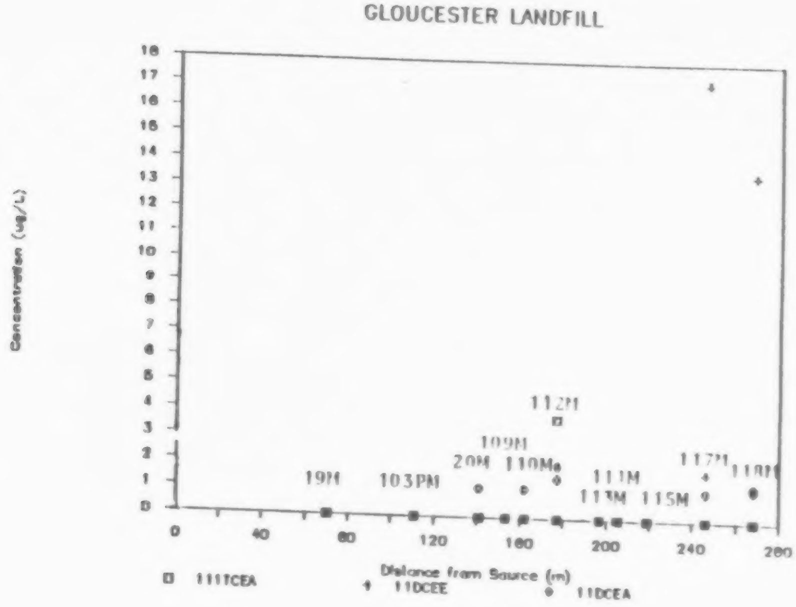
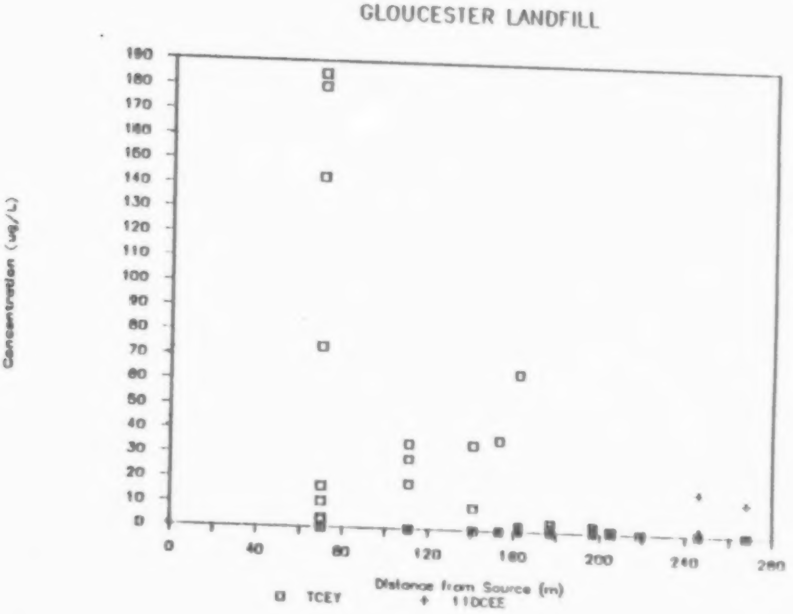


Figure 9: Eh vs. concentration chloride.





Figures 10 and 11: The concentrations of possible parent-daughter compounds through the middle of the plume.

EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHERN ONTARIO

by

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ABSTRACT

Organic liquids, less polar than water, are capable of producing dramatic changes in the structure of clayey soils and their hydraulic conductivity. Double layer theory is adequate to explain the behaviour of pure liquid-clay mixtures, however, it fails to fully account for the behaviour of water-compacted clays sequentially permeated by water and organic liquids. The "hydrophobic" nature of non-polar liquids such as cyclohexane and benzene, restricts their flow to larger channels through the pore system, resulting in decreases in **k** and with little effect on the double layers of water. The values of **k** seem to be dependent on the hydraulic gradient applied (non-Darcian behaviour) and threshold gradients may be measured below which breakthrough and flow do not occur. Viscosity plays an important role on the behaviour of water-soluble permeants such as ethanol, producing an initial decrease followed by gradual increases in **k** to equilibrium values that are practically independent of the hydraulic gradient used.

The addition of organic liquids induced rapid flocculation of the otherwise stable suspended matter in domestic waste leachate, the rate of flocculation being more pronounced with increasing abundance of organic liquids. Inorganic salts also precipitated resulting in a decrease in salinity of the clear leachate phase. The physical location of the flocs (as floaters or sinkers) depends on the amount and type of organic liquid added. Solubility limits mean that large amounts of most non-polar organics will generally produce two liquid phases.

Preliminary testing on water-compacted brown Sarnia soil using the clear phase of domestic leachate containing up to 45% ethanol and 5% benzene has yielded no significant increases in k. Furthermore, leachate spiked with 20% ethanol produced a decrease in **k** that is believed to be due to its higher viscosity. Mercury intrusion porosimetry results are presented to illustrate the very different soil fabric produced by moulding with organic/water mixtures compared to pure water.

INTRODUCTION

This paper reports on the results and problems encountered during the first year of study on the effects of organic liquids in domestic waste leachate on the hydraulic conductivity of southern Ontario brown soils. This presentation should be read in association with a preliminary paper presented by Quigley and Fernandez (1985) in the Proceedings of the 6th Technology Transfer Conference sponsored by the Ontario Ministry of the Environment. The nature of the Sarnia test soils and the importance of organics was outlined in the preliminary paper.

ORGANIC/LEACHATE INTERACTION

Flocculation and Phase Separation

Initial experiments involved addition of relatively large amounts of organic liquids to domestic waste leachate from London's Westminster landfill site. A schematic drawing of these mixtures after sitting for 18 hours is shown on Figure 1. The hatched regions represent the dark brown flocs, the dotted zones represent stable suspended matter and the open zones represent clear liquid. Except for influent 1 in Bottle #1, which was untreated leachate, the clear liquid phase in each mixture was separated and used as a permeant in hydraulic conductivity tests, as described by Quigley and Fernandez (1985). In mixtures 2 and 3 only one liquid phase is present due to the complete solubility of ethanol in the leachate. The stable suspended matter in the raw leachate (Bottle #1) is flocculated upon addition of ethanol, the flocs then settling to the bottom as shown by Bottles 2 and 3. In mixture 4, the flocs are "dragged" upwards by benzene resulting in an upper "benzene rich" phase and a lower aqueous phase. It appears from the scale dimensions in Figure 1 that the amount of suspended sediment that flocculates increases with increase in the amount of organic liquid. Also, the physical location of the flocs (as floaters or sinkers) appears from Figure 1 to be a function of the amount and type of organic liquid added.

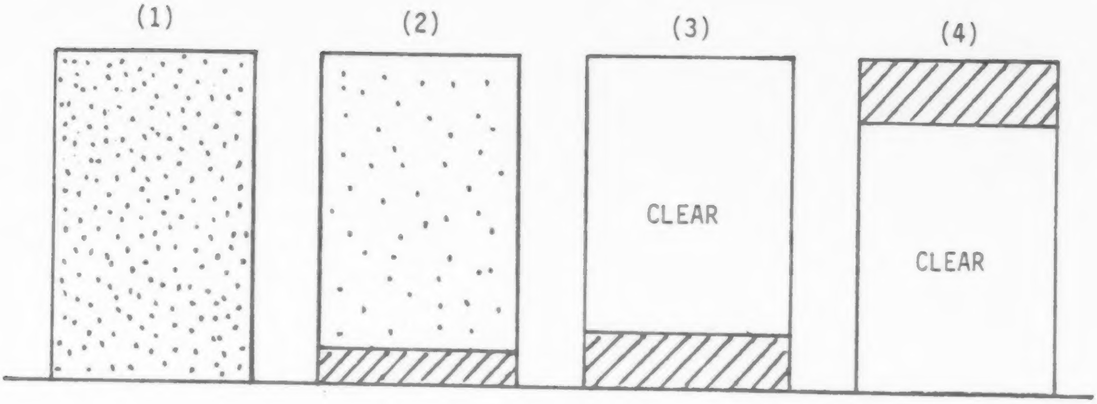

FIGURE 1. LEACHATE/ORGANIC MIXTURES AT 18 HOURS

(1)	100% LEACHATE.	DARK BROWN STABLE DISPERSED SUSPENSION
(2)	80:20 LEACHATE:ETHANOL.	DARK BROWN FLOCS AT BOTTOM OF MEDIUM BROWN SEMI-CLEAR SUSPENSION
(3)	60:40 LEACHATE:ETHANOL.	DARK BROWN FLOCS AT BOTTOM OF CLEAR SOLUTION
(4)	40:50:10 LEACHATE:ETHANOL:BENZENE.	MEDIUM BROWN FLOCS FLOATING ON CLEAR SOLUTION

Although the flocculation resulting from addition of organics surprised us, it is totally logical chemically, and considerable work is now under way to establish what components of the original leachate separate out with the flocculated phase. The results of our preliminary work are presented in four tables in Appendix A.

Viscosity Alteration

During start-up of this project, we discovered that dramatic changes in solution viscosity occur when alcohols and water are mixed. Figure 2 illustrates this well known chemical phenomenon for mixtures of both methanol and ethanol in water at 20°C. The ratio of mixture viscosity to water viscosity increases with increasing alcohol content to a maximum at an alcohol content of about 40%. As the alcohol content is increased beyond 40%, the viscosity decreases to values for pure alcohol. It is clear from Figure 2 that, up to about 25% alcohol content, the increase in the viscosity is more pronounced for ethanol than for methanol. The influence of these viscosity changes on the hydraulic conductivity is discussed in the next section.

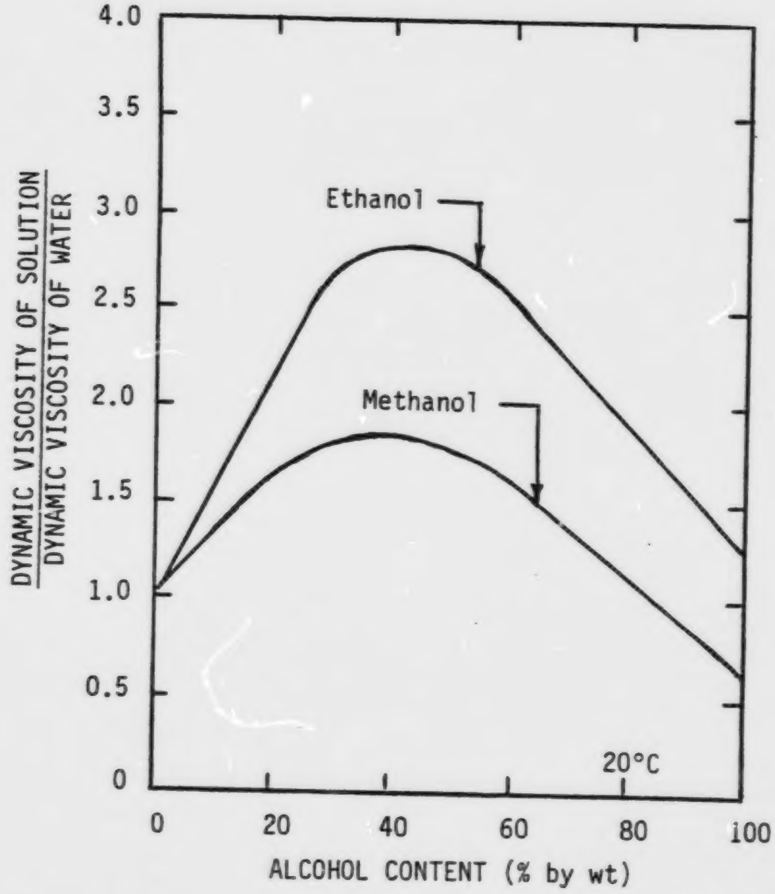

FIGURE 2. RELATIVE VISCOSITY OF AQUEOUS SOLUTIONS CONTAINING ALCOHOLS (Handbook of Chemistry and Physics, CRC, 56th Edition)

HYDRAULIC CONDUCTIVITY

Previous Work

Figure 3, taken directly from Bowders et al (1986), shows that the variation in hydraulic conductivity of compacted kaolinite permeated with solutions of varying amounts of methanol in water may be related to the viscosity curve for methanol shown on Figure 2. It is clear that for both fixed-wall and flexible-wall cells, the hydraulic conductivity decreases as the permeant becomes more viscous

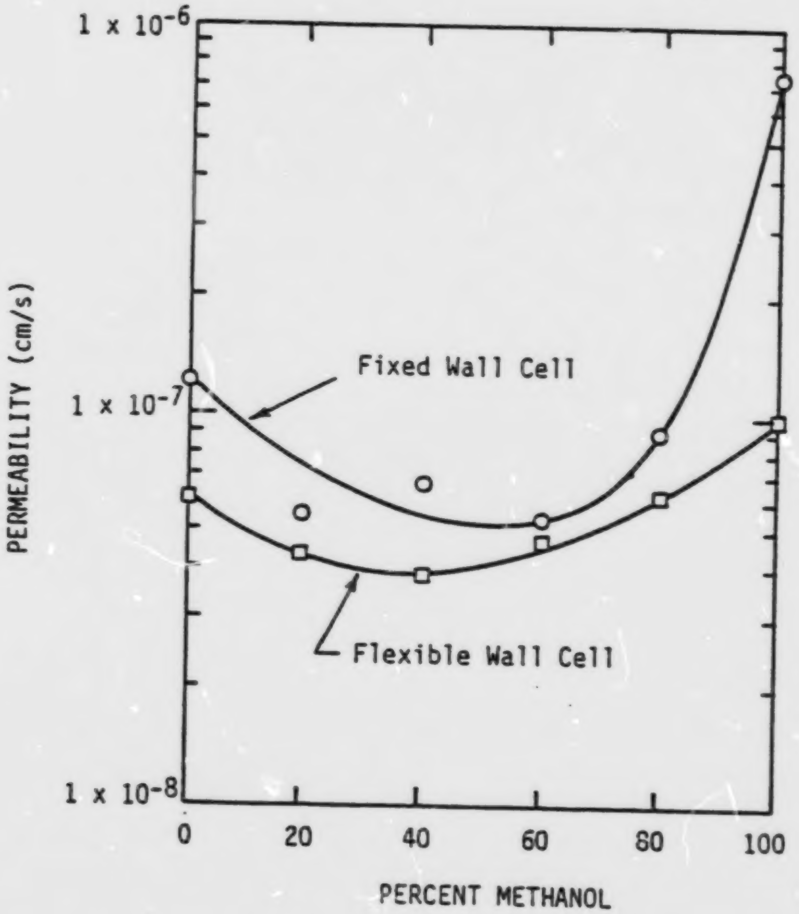

FIGURE 3. PERMEABILITY OF COMPACTED KAOLINITE TO AQUEOUS SOLUTIONS CONTAINING METHANOL (Directly from Bowders et al, 1986)

due to the addition of methanol. When the methanol content of the permeant exceeds 50% or so, the viscosity of the permeant decreases again and flow through the pores increases. The hydraulic conductivity obtained from the fixed-wall cell is higher than that obtained from the flexible-wall cell, irrespective of the methanol content of the permeant. This may be explained by flow along the sides of the fixed-wall cell. In our experiments, an effective stress is applied to the soil and lateral yield has successfully prevented side-wall leakage.

The hydraulic conductivity, k (cm/s) of the same kaolinitic soil permeated with methanol/water mixtures is replotted on Figure 4a. When the effects of viscosity are removed by plotting the intrinsic permeability, K (cm^2) the soil shows little change in K as the amount

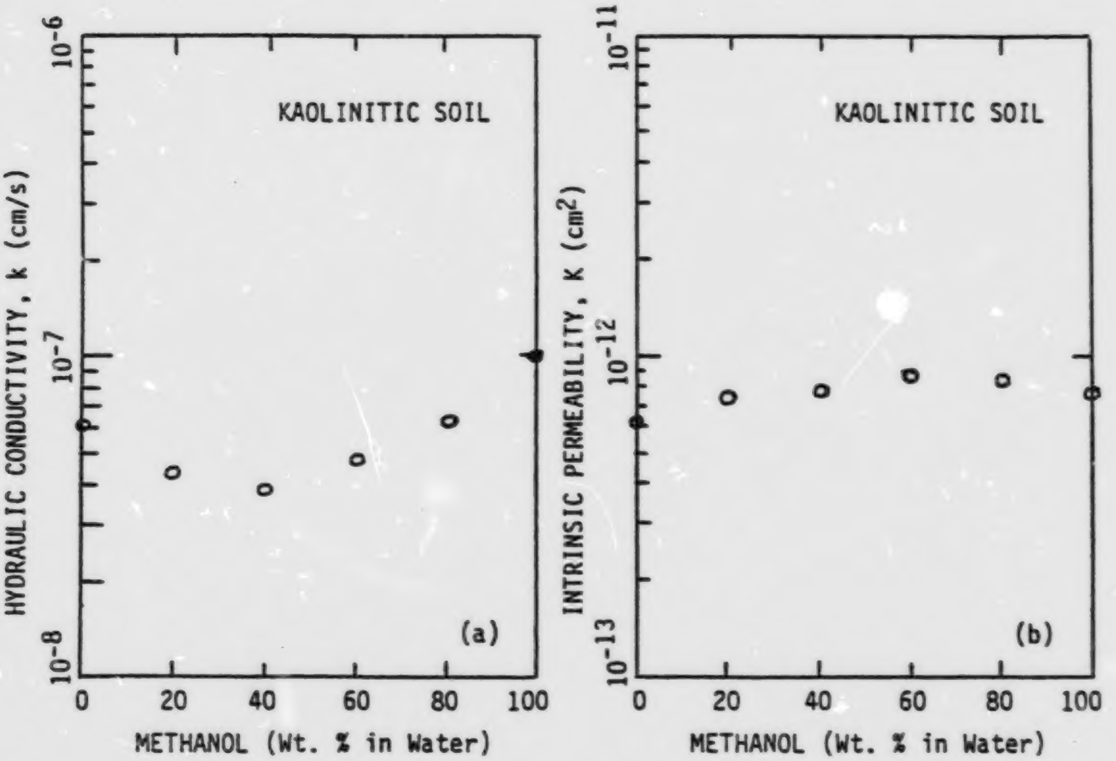

FIGURE 4. HYDRAULIC CONDUCTIVITY AND INTRINSIC PERMEABILITY VS PERCENT METHANOL IN WATER (a) DIRECTLY FROM DANIELS & LILJESTRAND, 1984; (b) REPLOTTED FROM DANIELS & LILJESTRAND, 1984

of methanol in water is increased from 20 to 80 percent (Figure 4b). Clearly for this inactive soil, viscosity changes control the changes in hydraulic conductivity, and not changes in the behaviour of the clay itself.

Current Hydraulic Conductivity Studies

Water/Alcohol/Clay Systems

Similar plots obtained for the Sarnia brown clayey silt compacted at a constant void ratio of 0.80 are shown in Figures 5a and 5b. A major difference in compaction procedures was employed, however, the soil being compacted and permeated with the alcohol/water mix shown. Figure 5a shows that up to about 40% ethanol, the hydraulic

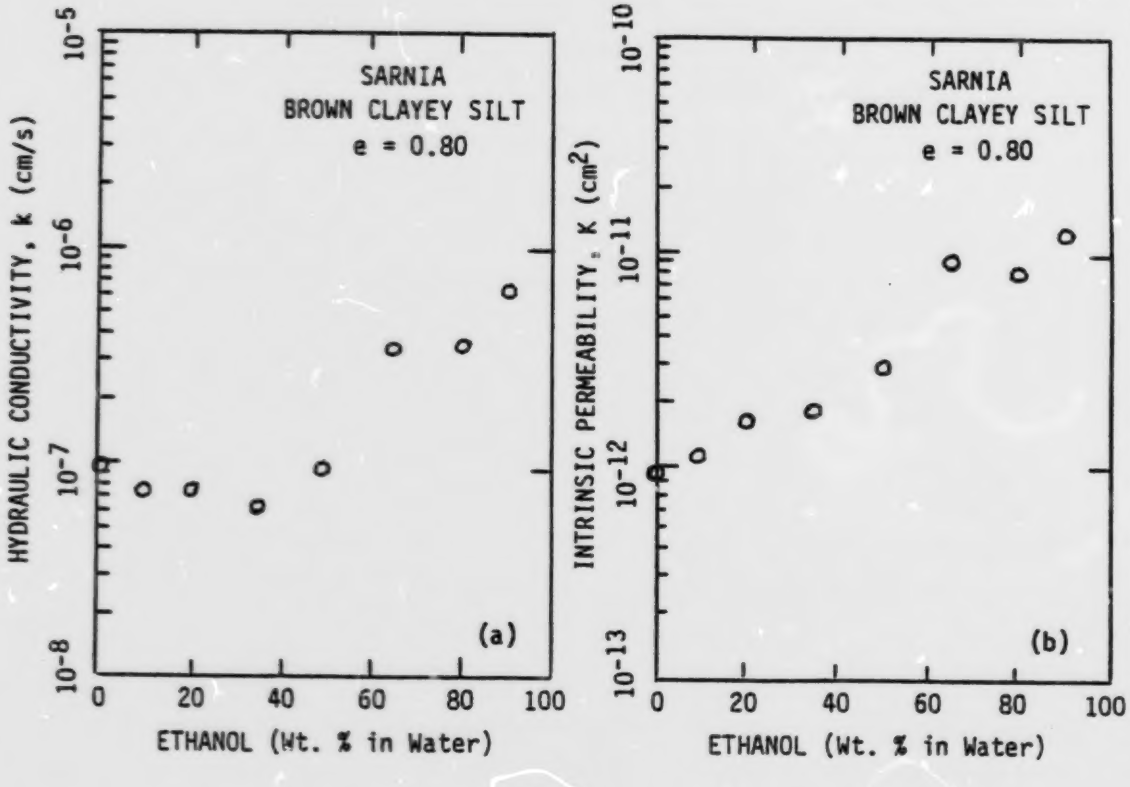

FIGURE 5. HYDRAULIC CONDUCTIVITY AND INTRINSIC PERMEABILITY VS PERCENT ETHANOL IN WATER (COMPACTED AND PERMEATED WITH MIX SHOWN)

conductivity decreases slightly and then increases by nearly an order of magnitude as the amount of ethanol was increased to 90%. The companion plot of intrinsic permeability vs percent ethanol in water (Figure 5b), however, shows an increase in K with increasing amounts of ethanol in water. Thus the Sarnia brown clayey silt, rich in illite, chlorite and smectite behaves differently from the kaolinitic soil used by Daniels and Liljestrand (1984). Since the kaolinitic soil is believed to have been compacted with water and then permeated with the water/alcohol mixtures the results are not strictly comparable to the Sarnia soil results. This matter is discussed further in the porosimetry section.

The rapid increase in intrinsic permeability (Figure 5b) is believed to be due to double layer contraction by the presence of alcohol (lower dielectric constant than water) plus soil flocculation and ped/macropore formation prior to and during compaction.

Leachate/Alcohol/Clay Systems

Four hydraulic conductivity tests carried out on water compacted soils, using the selected permeants described in the previous sections are shown on Figures 6 to 9. The soil was brown silty clay from 0.3 m depth whose clay minerals consist mainly of illite, chlorite and up to 10% smectite (see detailed composition in Quigley and Fernandez, 1985).

Figure 6a (adapted from Quigley and Fernandez, 1985) indicates that natural domestic landfill leachate causes a slight decrease in **k** from $\sim 2.0 \times 10^{-9}$ cm/s to $\sim 1.8 \times 10^{-9}$ cm/s (leachate) in spite of extensive K^+ fixation and retardation shown by Figure 6b. The retardation of Na^+ and K^+ results in desorption of Ca^{++} and Mg^{++} resulting in effluent concentrations far above influent values.

On Figure 7a, the results of testing using leachate spiked with 20% ethanol as the permeant are presented. They indicate that **k** decreases from $\sim 5.4 \times 10^{-9}$ cm/s (water) to 3.3×10^{-9} cm/s (spiked leachate). This small decline in **k** appears compatible with observed viscosity increases at this concentration of alcohol in water. The effluent ethanol concentration curve (Figure 7b) shows early arrival and some tailing indicating channel flow, although effective replacement of the original pore water by the ethanol-spiked permeant

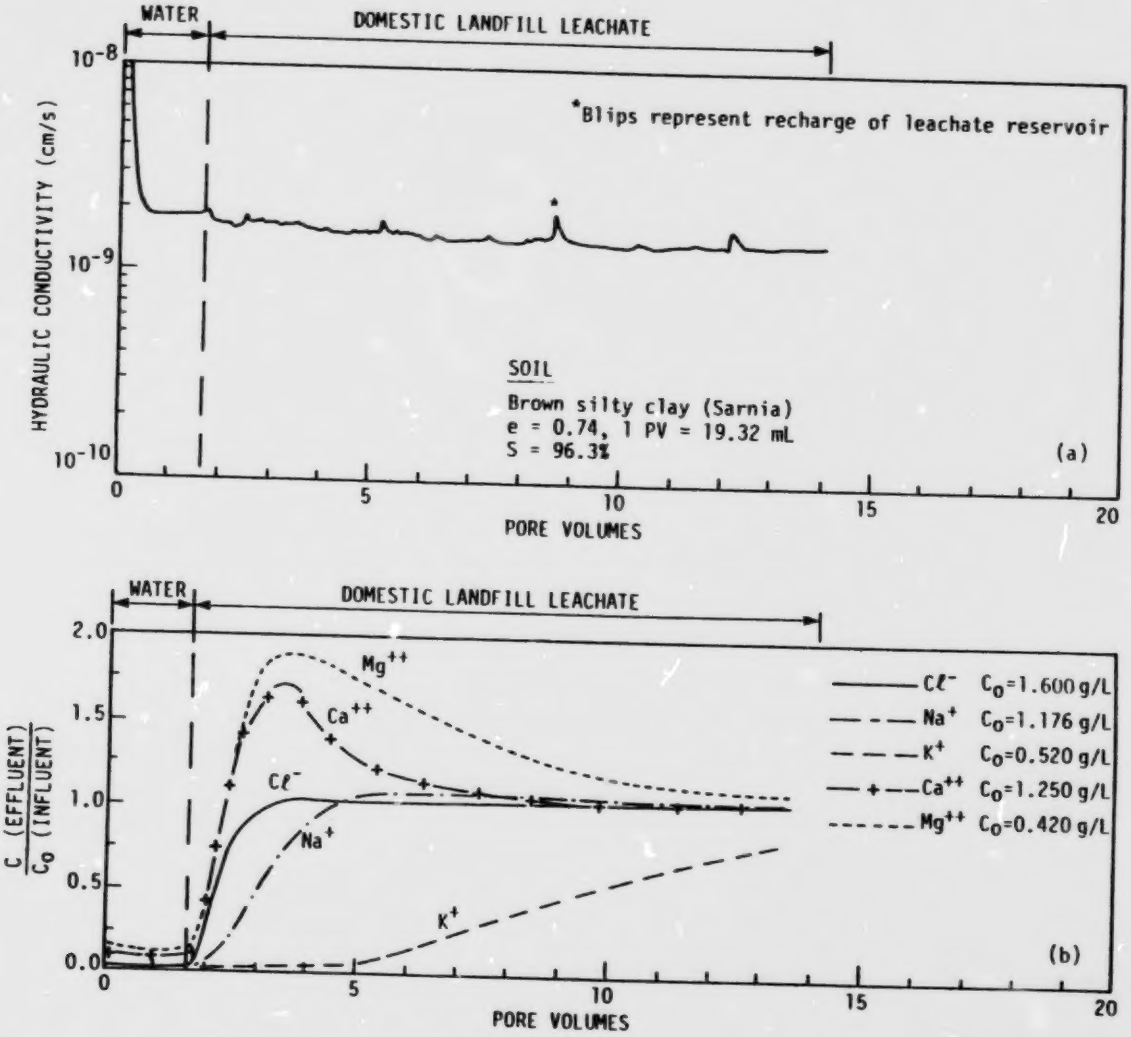

FIGURE 6. SOIL/DOMESTIC LEACHATE COMPATIBILITY: (a) HYDRAULIC CONDUCTIVITY, (b) EFFLUENT CHEMISTRY VS PORE VOLUMES OF LEACHATE; WEATHERED SARNIA SOIL, 0.3 m DEPTH, COMPACTED, VOID RATIO = 0.74

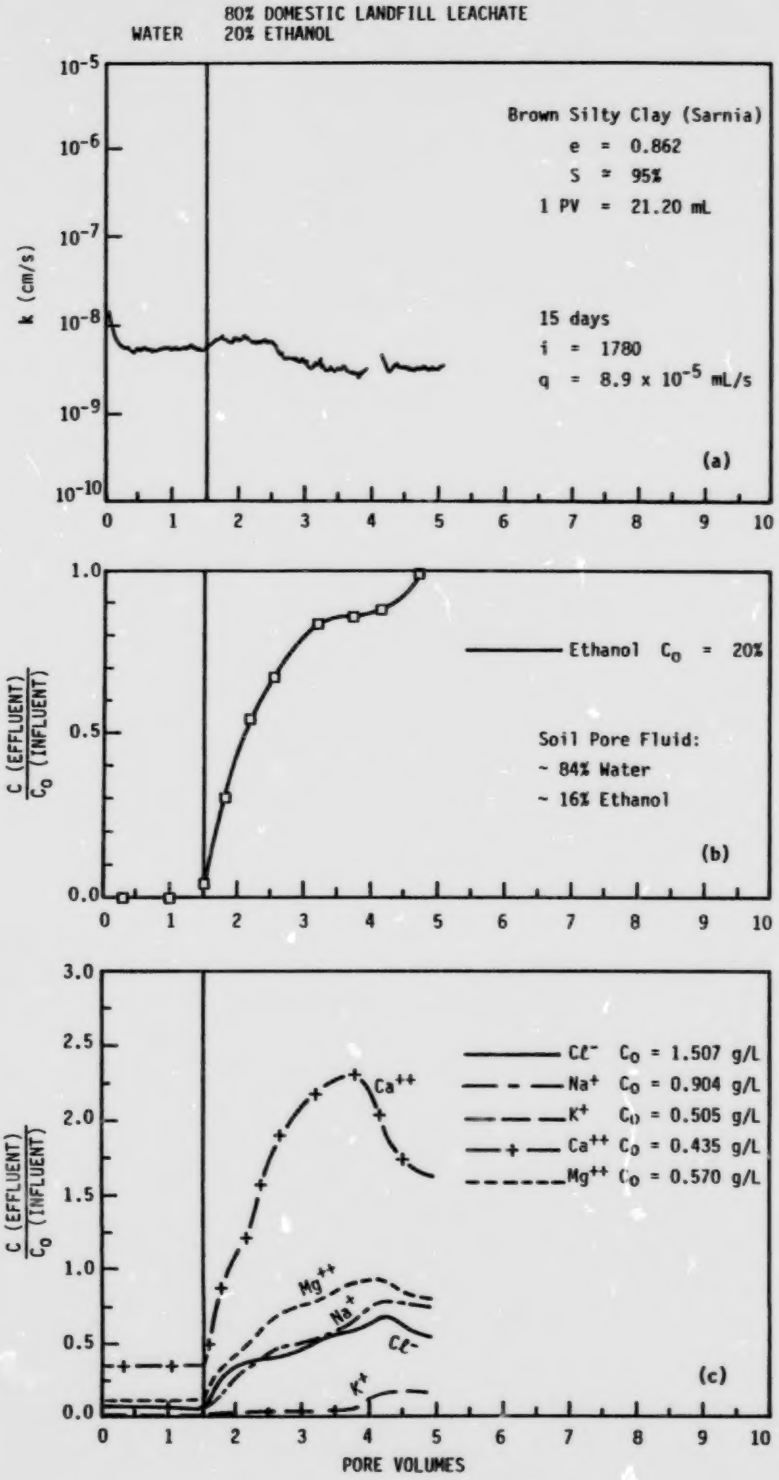

FIGURE 7. SOIL-LEACHATE COMPATIBILITY (PERMEANT 2); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

appears to have occurred. Post-testing analysis of the pore fluid (extracted by distillation from the soil revealed that it contained ~ 16% ethanol, which compares favourably with the 20% ethanol concentration of the influent leachate.

The test using leachate spiked with 40% ethanol as the influent permeant (Figure 8a) resulted in a slight increase in **k** from ~ 5.7 x 10^{-9} cm/s (water) to ~ 6.9 x 10^{-9} cm/s (spiked leachate). In contrast, the leachate spiked with 45% ethanol and 5% benzene produced a slight decrease in **k** from ~ 6.2 x 10^{-9} cm/s to ~ 4.0 x 10^{-9} cm/s after about 3 pore volumes of leachate flow (Figure 9a).

The effluent concentration curves for ethanol shown in Figure 8b and 9b are both similar to that for the leachate spiked with 20% ethanol (Figure 7b). The respective post-testing ethanol concentrations in the soil pore fluids are ~ 32% and ~ 36%. These values correspond to ~ 80% of the ethanol concentration in the respective influent indicating extensive replacement of the original pore water.

The effluent concentration curve for benzene (Figure 9b) displays an irregular pattern suggestive of evaporation losses in the effluent collection bottles. The C/C_0 for benzene reached 0.5 after 3.3 pore volumes of leachate flow and never did reach full influent values. The final benzene value in the pore fluid was only ~ 2% corresponding to less than 50% of the influent value.

The effluent concentration curves for Cl^- and soluble cations (Na^+, K^+, Ca^{++} and Mg^{++}) are presented in Figures 6c, 7c, 8c and 9c. The curves for the present series of tests (Figures 7c, 8c and 9c), in particular, illustrate the following features:

a) Potassium is strongly attenuated and C/C_0 does not exceed 20% of the corresponding influent values. This behaviour is akin to that shown by pure landfill leachate (Figure 6c).

b) The sodium and chloride curves show an irregular and strongly tailed behaviour indicating channel flow.

c) The early arrival and "hardness halo" effect shown by calcium and magnesium for pure leachate (Figure 6c) is

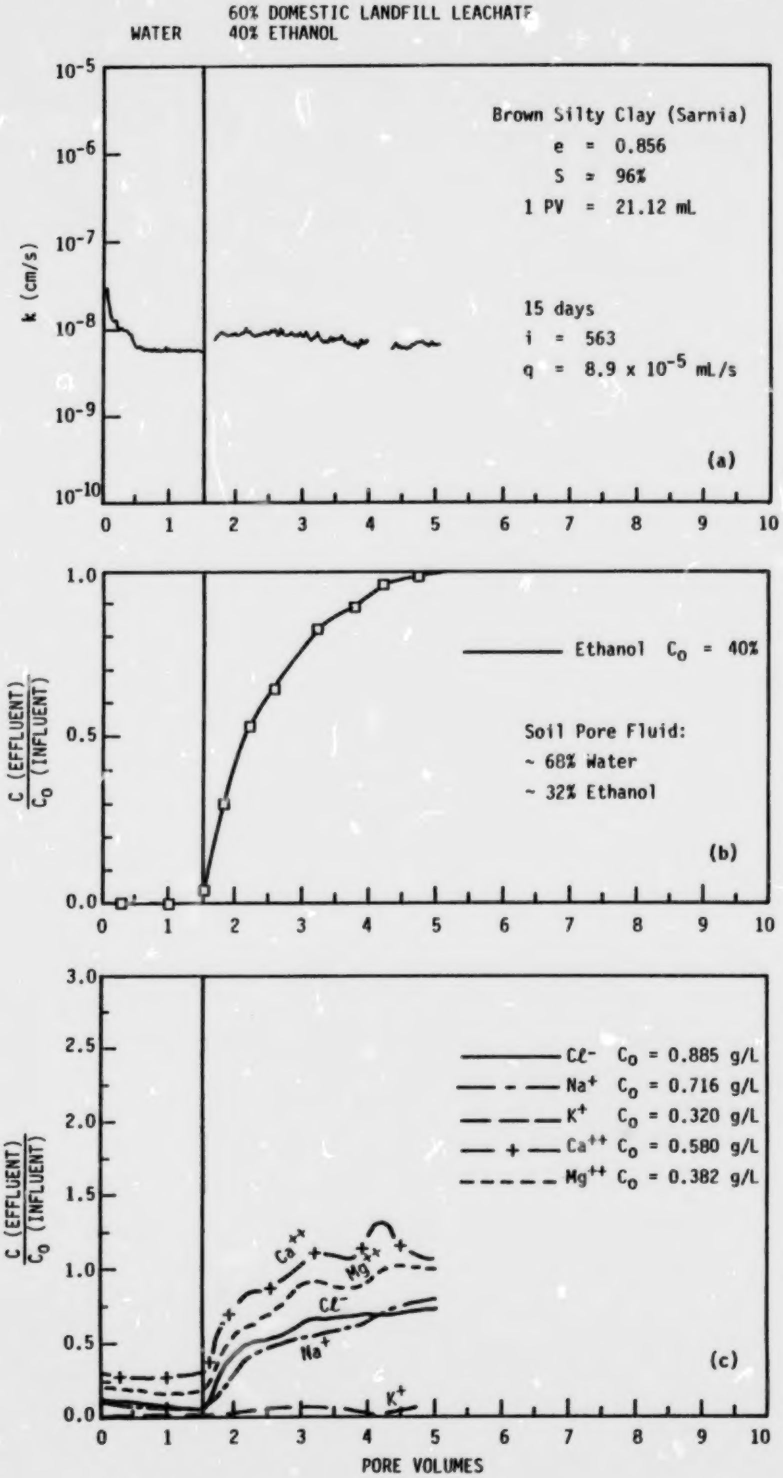

FIGURE 8. SOIL-LEACHATE COMPATIBILITY (PERMEANT 3); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

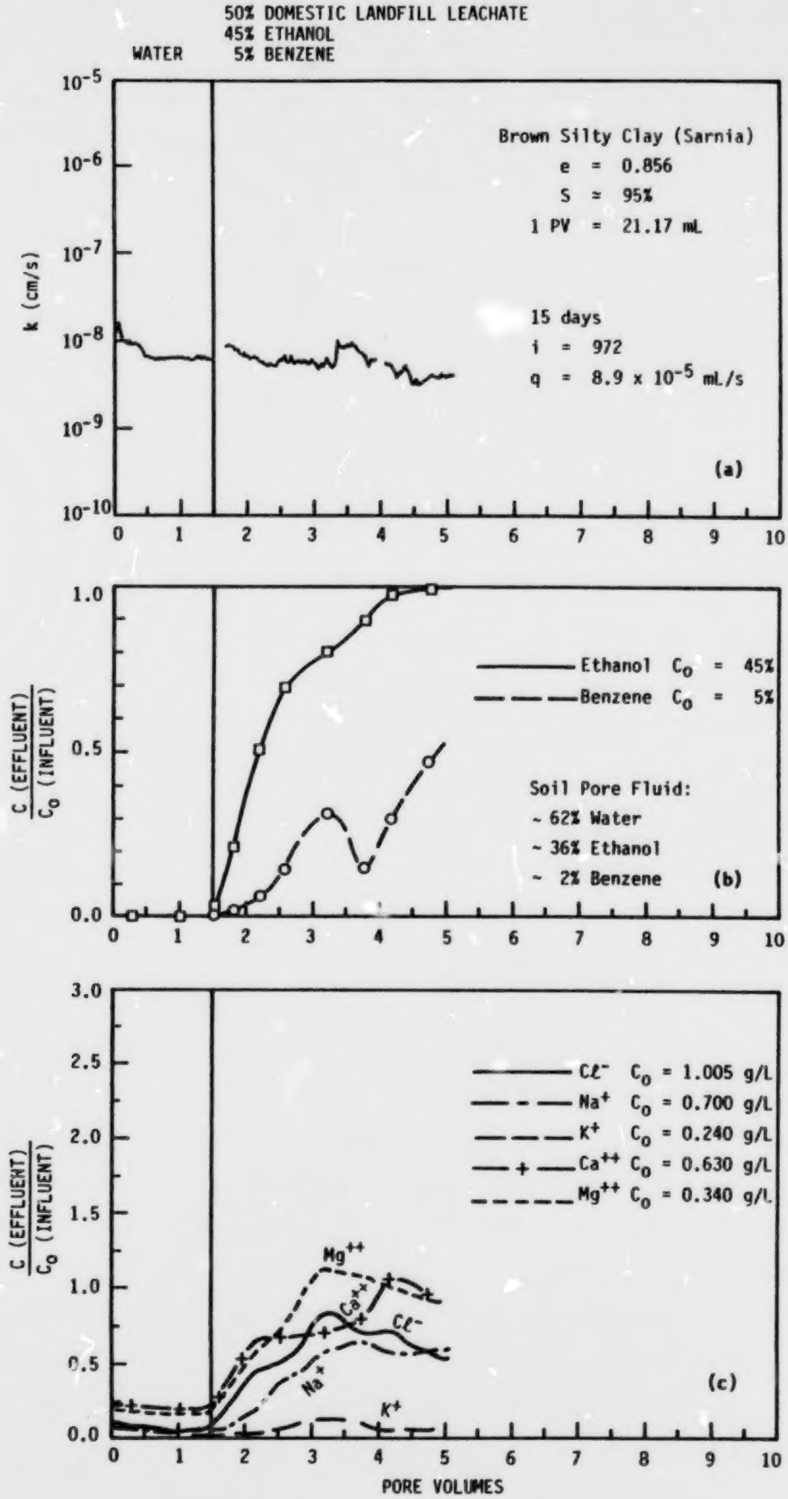

FIGURE 9. SOIL-LEACHATE COMPATIBILITY (PERMEANT 4); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

exhibited only by calcium in the sample permeated with leachate spiked with the least amount (20%) of alcohol (Figure 7c). At higher alcohol contents, the desorption of Ca^{++} and Mg^{++} appears to be strongly muted. Inspection of influent permeant composition (Table I, Appendix A), however, indicates that the Na^+ and especially K^+ are greatly reduced from the original leachate values due to the addition of alcohol. The intensity of desorption may have been reduced in large part by the reduction in alkali content of the influent. Ion balance calculations had not been performed at the time of preparation of this paper.

POROSIMETRY CONTROLS

The engineering behaviour of clayey soils is controlled in large measure by the soil structure inherited from its depositional environment. Compacted soils are similar in that the moulding liquid mixed with the soil before compaction should have a greater effect on fabric and soil structure than many post-compaction permeants.

For example, the Sarnia soils compacted with pure water and then permeated with 20% ethanol/80% leachate yielded a single, very dominant pore size mode of 0.08 μm as shown on Figure 10. The mode itself was defined by high pressure mercury intrusion into freeze-dried samples. When the same soil was compacted with 10% ethanol/90% water, the major pore size mode increased to 0.24 μm with a very broad range of smaller pores (Figure 11). Finally, a moulding fluid of 65% ethanol/35% water yielded a very flocculated structure with some large pores such as that shown by the minor mode at 16.13 μm on Figure 12.

It is these large interped pores which probably produced part of the increased **k** values shown on Figure 5 for the higher alcohol contents in the influent aqueous solutions.

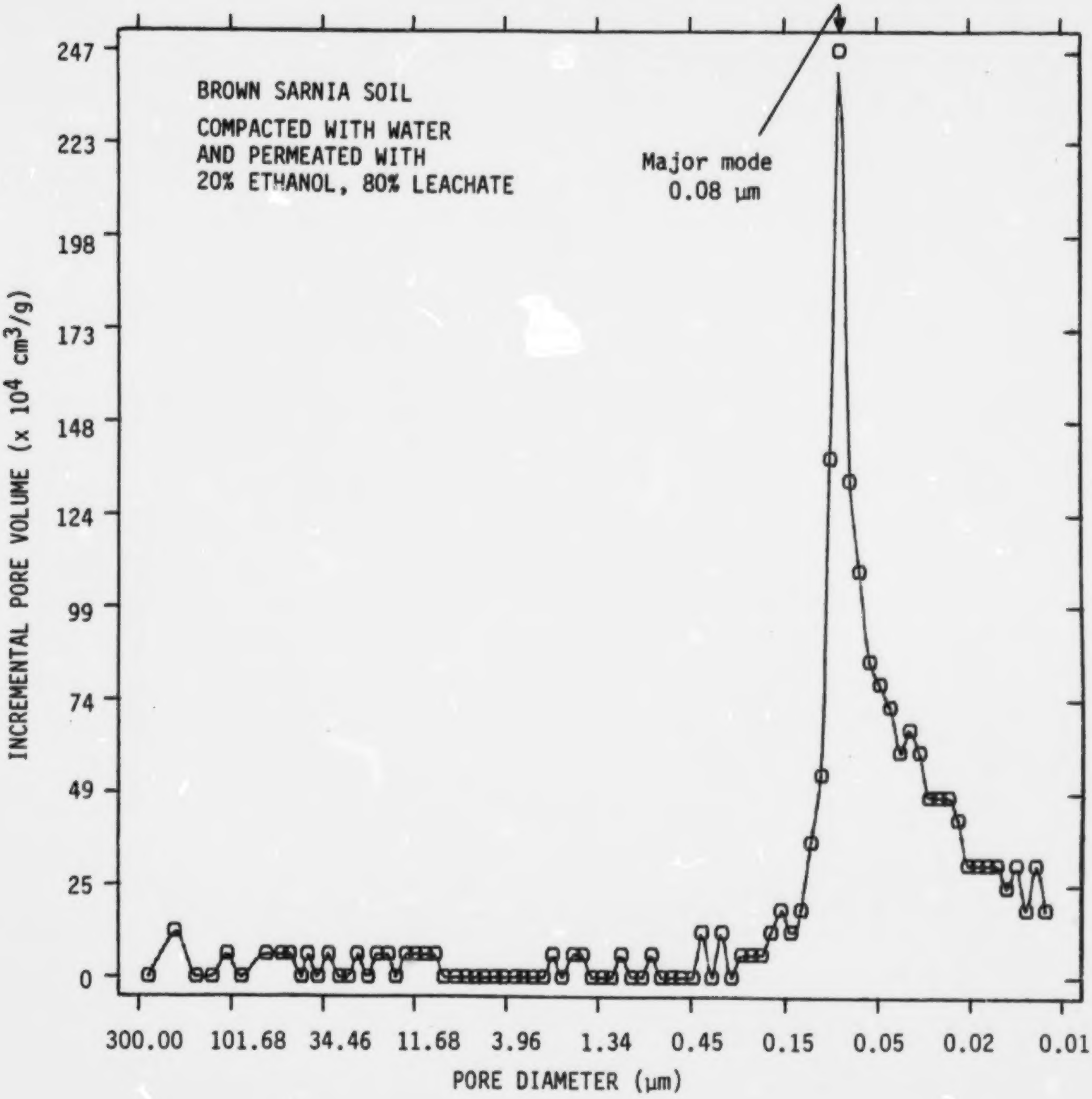

FIGURE 10. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED AND COMPACTED WITH WATER THEN PERMEATED WITH MIXTURE OF 20% ETHANOL AND 80% LEACHATE

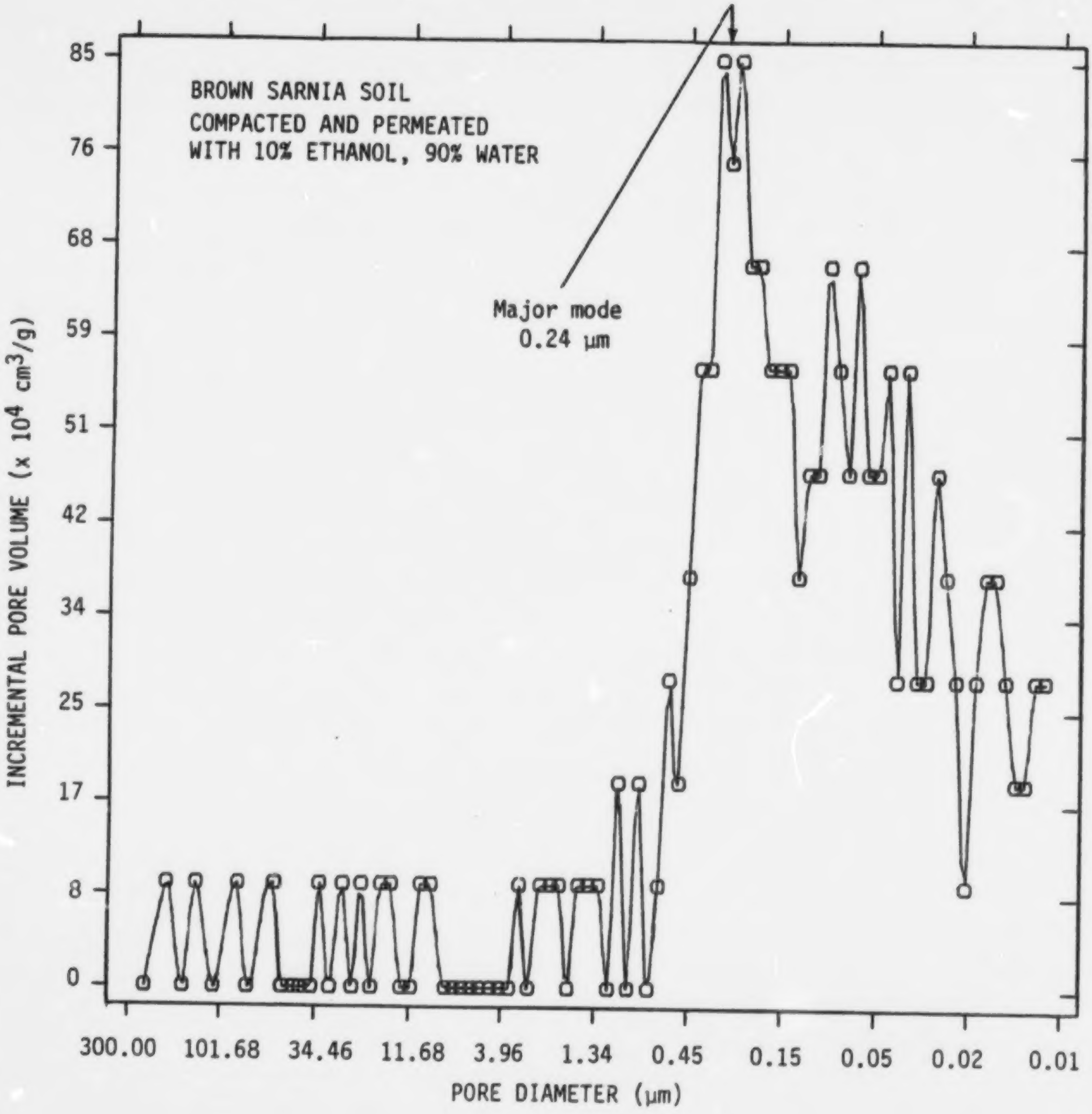

FIGURE 11. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED, COMPACTED AND PERMEATED WITH 10% ETHANOL AND 90% WATER

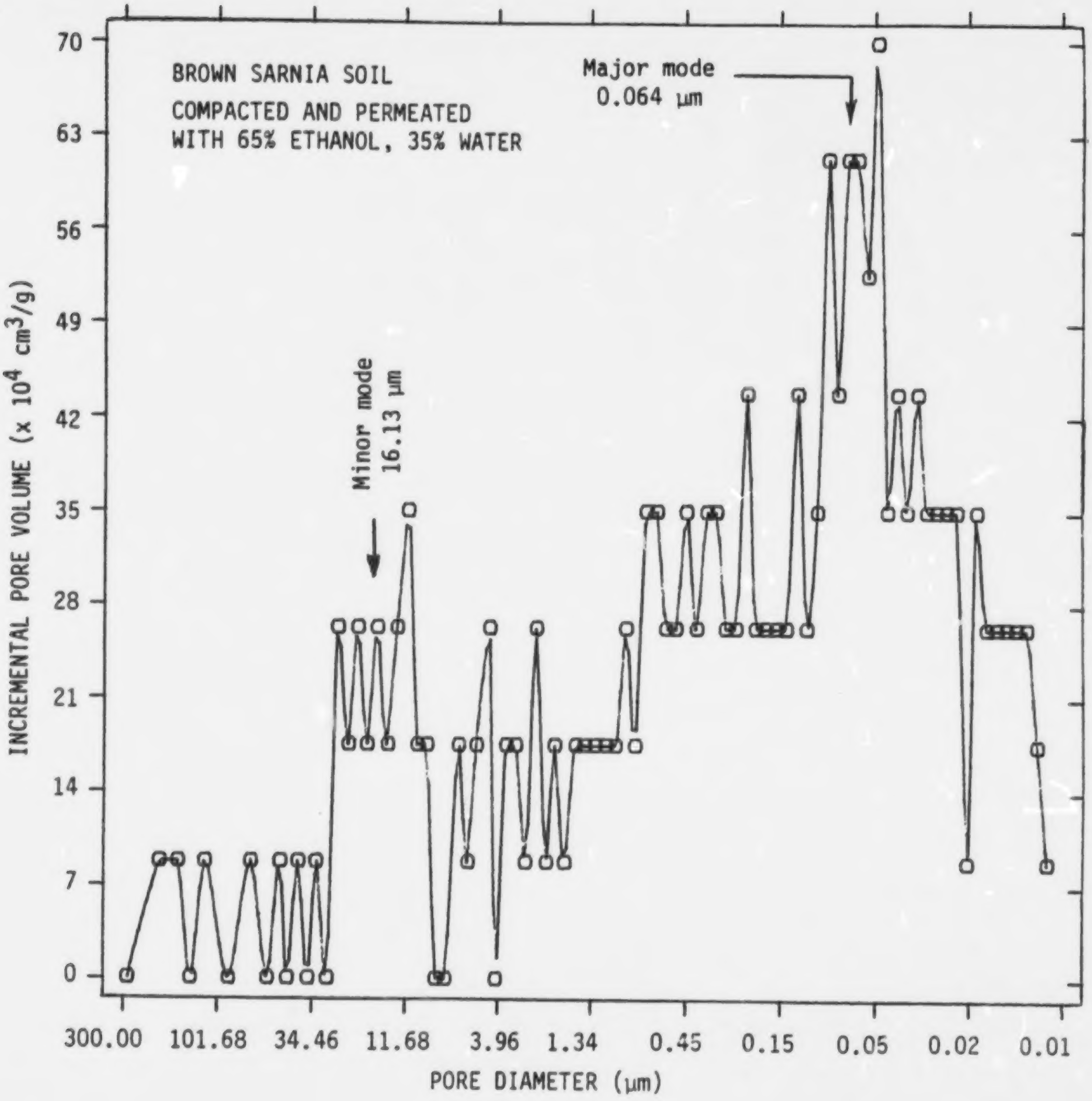

FIGURE 12. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED, COMPACTED AND PERMEATED WITH 65% ETHANOL AND 35% WATER

CONCLUSIONS

Although the work is still at a very preliminary stage due to unexpected interaction between the leachate and organic liquids, a few general conclusions may be drawn.

1. Raw leachate tends to flocculate on addition of alcohol producing semi-clear to clear supernatant liquids above "sinker" flocs. Addition of benzene with the alcohol caused the flocs to float.
2. Significant decreases in effluent salinity occur with the addition of alcohol.
3. Up to 50% alcohol added to leachate caused decreases in **k** primarily due to increased influent viscosity.
4. Moulding the clay in alcohol-bearing leachate is probably not a good idea since resultant flocculation appears to create large interped pores not as prominent in water moulded (dispersed) clays.

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APPENDIX A

TABLES OF LEACHATE COMPOSITION AND PROPERTIES

TABLE I. CHEMICAL COMPOSITION OF THE PRIMARY PERMEANT

Primary Permeant	Chemical Composition (% by weight)		
	Leachate	Ethanol	Benzene
1	100	0	0
2	80	20	0
3	60	40	0
4	40	50	10

TABLE II. CHEMICAL CONSTITUTION AND IONIC SPECIES CONCENTRATION OF THE SELECTED PERMEANTS

Selected Permeant	Chemical Constitution (% by wt.)			Ionic Species in Influent (g/L)					
	Leachate	Ethanol	Benzene	Sodium	Potassium	Calcium	Magnesium	Iron	Chloride
1	100	0	0	1.088	0.776	0.724	0.620	0.032	1.466
2	80	20	0	0.904	0.505	0.435	0.57[illegible]	0.020	1.507
3	60	40	0	0.716	0.320	0.560	0.382	0.005	0.885
4	50	45	5	0.700	0.240	0.630	0.340	<0.001	1.005

TABLE III. VISCOSITY AND DENSITY OF THE SELECTED PERMEANTS

Selected Permeant	Density, ρ (g/cm^3)	Dynamic Viscosity, μ (centipoise)
1	1.0020	1.160
2	0.9704	2.091
3	0.9435	3.866
4	0.9312	2.822

TABLE IV. FLOC COMPOSITION

Permeant	Ionic Species (% by weight)					
	Sodium	Potassium	Calcium	Magnesium	Iron	Total
2	5	3.5	13.5	3.5	8	33.5
3	5	3.5	15	3.5	10	37
4	5	3	20	3.5	9	40.5

Evaluation of the impact of shock loading on the microbiota of the Welland River

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ABSTRACT

The specific conductivity of composite samples from two industrial discharges was compared to their continuous conductivity records. The composite samplers failed to adequately represent periods of shock loading. These shock loads were 2 to 3 times the average concentration of electrolytes in the industrial discharge.

It was concluded that composite samplers typically fail to reflect shock loading events and are therefore unacceptable instruments for monitoring temporal changes in industrial discharges to the environment where protecting the natural biota is the primary aim of the monitoring program.

The attached microbiota in rivers provide water managers and those entrusted with the protection of the organisms inhabiting our rivers with a built in continuous monitoring system. Waterways exposed to infrequent episodes of toxic effluent discharge (i. e. shock loading) will have a microbiota which is nearly as impoverished as the microbiota of continuously polluted waterways. Thus sporadic sampling of the water by water quality personnel and those employing composite samplers frequently fails to indicate the true water quality conditions in the area. The natural microbiota which serve as continuous monitors of water quality and continuous recording conductivity meters are far more reliable indicators of water quality than are composite samplers.

INTRODUCTION

In general, any rapidly increasing delta-type pulse which affects the chemical or physical environment of a natural area for a brief period of time can be classified as a shock load (Von Tumling 1968, Dickman 1973). When the species composition and diversity of attached algae are used to characterize the severity of an industry's discharge, a small volume polluter practicing shock loading will register an impact to the environment far greater than the volume and toxicity of its discharge would suggest. In some cases this impact will be equal to that of a large volume polluter which discharges continuously without shock loading (Dickman 1975). For example, in 1972-1974 the Canadian International Paper Company Ltd. (C.I.P.) pulp mill discharged annually approximately ten times the volume of the E. B. Eddy Co. Ltd. pulp mill. Nevertheless, the Ottawa River downstream of the E. B. Eddy Co. (during E.B. Eddy shock loading episodes) reached concentrations similar to those attained by C.I.P. during its normal loading conditions (Dickman 1975). Even though these shock loads from the E. B. Eddy Co. were infrequent, the attached algal community downstream of that company was as impoverished as the one downstream of C.I.P. (Ibid.). Thus it was concluded that the sporadic dumping by the E. B. Eddy Co. was as detrimental to the downstream microbiota as the continuous dumping of a much larger volume of effluent by C.I.P.

The significance of this conclusion is important to environmental agencies entrusted with monitoring the effects of industrial discharges on the natural biota of our lakes and streams. To date, most Canadian environmental agencies and industries have persisted in collecting composite samples rather than continuous samples (Dalrymple 1985). Composite samplers such as the ones used by the Ontario Ministry of the Environment fail to reveal peaks or shock loading events.

In this paper, we will examine the consequences of using a continuous recorder in place of a composite bucket-type sequential sampler as a means of gauging water quality conditions in terms of electrolytic shock loading. It must be emphasized that the primary focus of this study was directed toward the analysis and the protection of the natural biota of the wetlands portion of the lower Welland River where it flows into the Niagara River (Figure 1) and thus to Lake Ontario. It is recognized that all substances borne by the Welland River impact directly on the Niagara River and Lake Ontario (Dickman et al., 1983; Kaiser et al., 1983; Comba & Kaiser, 1984).

METHODS

Specific conductivity meters respond to the concentration of electrolytes in the water. A continuous recording Model SI-1 Lisle Specific Conductivity meter was installed below the Cyanamid Canada Inc. Chemical Company near the confluence of Thompson's Creek (Fig. 1, Station No. 4). Concomitantly, a YSI Instruments Co. battery operated specific conductivity meter was employed upstream at Station No. 3. The two instruments were intercalibrated and cross checked at daily intervals. The same technique was also adopted at Stations 1 and 2 above and below the Atlas-Mansfield outfall (Fig. 1). Peaks in specific conductivity below these two outfalls which did not occur upstream were assumed to result from shock loading discharges of electrolyte containing effluents. Both Atlas Steels and the Diversitech General Company discharge into the Altas-Mansfield sewer while the Cyanamid Chemical Company is the only industry discharging large volumes of material into Thompson's Creek. The dates for monitoring the effluent being discharged into the Welland River by each of these industries were chosen at random. Attached algae (periphyton) from above and below these Welland River sites was removed by scraping an area of approximately 1 cm^2 using standard procedures (Wetzel 1964). Epipelic samples were taken by removing only the top 1-2 mm of the sediment on top of the mud. All epipelic replicate samples from each area were pooled and then homogenized. A 1 ml subsample was suspended in 10 ml of filtered tap water and placed in a sedimentation chamber with a few drops of Lugol's solution (Wetzel 1964). After sedimentation was complete (24 hr), the chamber was placed on a Leitz orthoplan inverted microscope stage and the microbiota enumerated by selecting 10 ocular fields at 150 X, 600 X and 1,500 X magnifications. Epiphytic samples were taken whenever Typha (cattails) or Phragmites (bullrushes) were present. An area of 1 cm^2 was scraped from near the waterline for each of three stems of these emergent aquatic macrophytes. These scraping samples were then pooled and analyzed as described above for the epipelic samples.

Counting procedures for the microbiota were similar to those described by Andrews and Lohmann (1972). Category one (rare taxa = 1-10 individuals per slide) was represented by the number 10, category two (10-200 individuals/slide) was represented by the number 200 etc. This procedure of presenting quantitative data as ranges (rare = 1-10 individuals per slide, 2 = moderate = 10-200 individuals per slide, 3 = common = 200 - 3,000 individuals per slide, and 4 = abundant = 3,000-40,000 individuals per slide) has been adopted by numerous scientists. Rounding off the number of significant figures to avoid indicating more precision than the data warrant is also recommended (Koivo and Ritchie 1978).

RESULTS

We monitored the Cyanamid discharge at station 4 on Thompson Creek (Fig. 1) on March 4, 1986 with our Lisle continuous conductivity meter. We then reviewed the data on the strip chart recorder and calculated what a one litre bucket type sequential composite sample taken every 15 minutes would represent in terms of its 12 hour composite sample (Table 1). During the same 12 hr. period the specific conductivity meter registered two shock loads with peaks of 2,150 and 1,780 microsiemens/cms (Fig. 2). The specific conductivity from the bucket sampler composite sample was calculated for purposes of comparision (920 microSiemens/cm).

The specific conductivity recorded at the Atlas-Mansfield outfall (Sites 1 & 2, Fig. 1) showed seven spikes (shock loads) during a 12 hr. period ranging from a low of 1,500 microSiemens/cm to a high of 5,000 microSiemens/cm (Fig. 2). Subsequent to this study which took place in June and July of 1986, the Atlas Specialty Steels Division shut down its Welland Plant in order to remedy this shock loading problem. In September and October, their discharge was again monitored and we concluded that over 80% of the shock loads had been eliminated by the remedial action taken by the Atlas Specialty Steels Division, Welland Plant.

Although the 12 hr mean conductivity at the Atlas-Mansfield outfall was only slightly higher than Cyanamid's, 12 hr mean (1,149 vs 920 microSiemens/cm) the peaks in the Atlas-Mansfield outfall conductivity record were far higher (5,000 vs. 2,150 microSiemens/cm), and far more frequent. The relationship this bears to the downstream microbiota is represented in Tables III and IV. The biotic diversity and species richness below both outfalls was compiled (Table V) from the data provided in Tables III and IV.

When the biotic diversity as reflected by both the Shannon-Weiner and Simpson diversity indices was regressed against distance downstream below the two outfalls, a significant ($p < 0.01$) correlation coefficient resulted (Table V).

DISCUSSION

Floristic Zonation Pattern

The distribution of higher aquatic plants below industrial outfalls was used as the basis for defining a zonation pattern to characterize the size of the impact and recovery zones below industries discharging toxic wastes into the Welland River (Dickman et al 1980). Immediately below a toxic waste outfall, a zone was encountered in which all higher aquatic plants were absent (impact zone; zone 1). Below the impact zone, three contiguous recovery zones were identified. The primary recovery zone (Zone 2) was characterized by tall emergent higher aquatic plants (HAP) (eg. *Typha* and *Phragmites*). The secondary recovery zone (Zone 3) was characterized by short HAP's (eg. *Pontederia*, *Sagittaria* and *Sparganium* as well as floating leaved HAP's (eg. *Potamogeton*, *Nuphar* and *Nymphea*). In addition, aquatic plants already noted for zone 2 were also present in zone 3. The tertiary recovery zone (Zone 4) was characterized by the presence for the first time of submersed HAP's (eg. *Elodea*, *Ceratophyllum* and *Myriophyllum*). A schematic representation of these 4 zones is provided (Fig. 3).

The relationship between the size of each of these zones and the toxicity and volume of effluents being discharged into it is the subject of an ongoing research program at Brock University. In general, the more toxic the effluent, the larger the size of the impact or dead zone below the discharge pipe. This relationship holds true regardless of whether the effluent is discharged continuously or sporadically.

Atlas-Mansfield Discharge

The effluent entering the Welland River at the Atlas-Mansfield sewer outfall was composed primarily of iron oxides and heavy metals. During periods of overflow, Atlas Steel's north and south waste treatment plant effluents, plus Diversitech's effluent, yard runoff and stormwater from the McAlpine municipal sewer was discharged into the Atlas-Mansfield Sewer (Dalrymple 1985 and Lindall Pers. Comm.). Atlas Specialty Steels, a division of Rio Algom Ltd., manufactures stainless steel alloys, dies, mold-blocks and die steel at its Welland River Plant. The raw materials for this production consists primarily of steel scrap, lime, ferrochrome, nickel oxide and ferro silicon (Ibid). Diversitech General Engineered Elastomers Division in Welland manufactures custom rubber compounds, mold bonded products, dense and sponge molded rubber, track bars and vibration isolation bushings.

The flow rate at the outfall of the Atlas-Mansfield sewer into the Welland River is approximately 30,000 m^3/day (Dalrymple 1985). Atlas Steels is a known source of chromium, iron, lead, nickel and zinc as well as phosphorus, nitrogen, sulphate, C.O.D., dissolved and suspended solids (Ibid). Diversitech is a known source of various rubber and plastic precursors. In April and May of 1986, oily wastes coated much of the downstream vegetation below the Atlas-Mansfield outfall. Other organic contaminants such as di and trichloroethylene were found only at trace levels by the Ministry of the Environment. Phenols were significantly higher at the Atlas 42" sewer manhole than in the Atlas intake water (Dalrymple 1985). As a result of these discharges a dead zone (zone 1) is associated with the outflow area of the Atlas-Mansfield storm sewer.

The first higher aquatic plant (Phragmites communis) which we encountered was located approximately 20 m below the Atlas-Mansfield Sewer outfall. Microflagellates, both heterotrophic forms (unpigmented colorless taxa, e.g. Sarcodina) and flagellated autotrophs (pigmented taxa) dominated the microbiota at this site (Table III). As one moved progressively further downstream into the secondary and tertiary recovery zones, the total number of species increased to 19 and the ratio of autotrophs to heterotrophs (ciliates, rhizopods and colourless flagellates) significantly increased ($P < 0.01$) over the same distance (Table III).

Cyanamid Impact

The Cyanamid Canada Inc. Welland River Plant has several outfalls to Thompson's Creek which carries their wastes into the Welland River approximately 4.5 km upstream of the Niagara River at Queenston (Fig. 1). Cyanamid manufactures a wide variety of nitrogen and phosphorus based chemical products including ammonia, urea, nitric acid, dicyandiamide, xanthate, cyphos animal feed, phosphates, guanidine, tetrabutyl-phosphonium pesticides and phosphine (Dalrymple 1985 and Draper, Pers. Comm.). The average flow from Cyanamid in 1981 was 19,200 m^3/day (1982 M.O.E. Data reported by Dalrymple 1985). On average, this 1981 daily discharge contained 184 kg phosphorus, 9,370 kg ammonia and urea nitrogen, 5,210 kg nitrate nitrogen, 5.57 kg free cyanide, 4.86 kg chromium, 1.78 kg nickel, 2.97 kg zinc and .113, .008, .064, .019, .008 kg of total phenols, arsenic, toluene, chloroform and naphthalene respectively (1981 EPS Data reported by Dalrymple 1985). Immediately downstream of the Cyanamid discharge pipes there is a dead zone in which no higher aquatic plants are able to survive. This dead zone (zone 1) extends from the Cyanamid discharge to Thompson's Creek for over 2 Km and on into the Welland River for a distance of 75 m along its north shore.

The large discharge of nitrogen-rich substances from Thompson's Creek into the Welland River at Station 4 has consistently stimulated the production of high numbers of the pollution tolerant flagellate, *Euglena convoluta* in the impact zone (Table IV, Dickman et al 1983). The number of heterotrophs and autotrophs were equal in the impact zone (8 taxa of each) and gradually the number of autotrophs increased downstream as the number of heterotrophs fell from 8 to 4 by the time the secondary recovery zone was reached. Total species richness increased from 16 taxa in the impact zone to 19 in the tertiary recovery zone (Table V). The Simpson Index increased from 0.48 in Zone 1 to 0.74 in Zones 4 and 5. The Shannon-Weiner Diversity index increased proportionately (Table V).

Shock Loading

The relationship between the biotic zonation pattern below an industrial outfall and the toxicity of that industry's discharge is complicated by the fact that few industries discharge their toxic wastes in a continuous fashion. Shock loading is the rule rather than the exception (Dickman 1975). When a large dead zone and a large recovery zone is discovered downstream of an effluent pipe that is not discharging a toxic waste, the possibility of shock loading should be investigated. To this end a continuous monitor rather than a composite sampler is recommended.

In conclusion, continuous monitoring and the use of natural in-stream biological monitors should replace sporadic spot samples and composite sampling in all water quality programs which have as their primary goal, the protection of the natural biota of our lakes and rivers. Where pont source discharges contain electrolytes, continuous specific conductivity monitoring permits a better understanding of the resulting downstream distribution of microbiota and higher aquatic plants. If a continuous conductivity recorder was coupled to a composite sampler so that samples were taken only during periods of shock loading, we feel that the analysis of these samples would improve our ability to interpret the distribution of the biotic assemblages located downstream of industrial outfalls.

ACKNOWLEDGEMENTS

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Table Captions

Table I	Continuous recording specific conductivity quarterly hour values of the conductivity of the water in Thompson's Creek near its confluence with the Welland River (4 March 1986, 12 noon to 12 midnight).
Table II	Continuous recording specific conductivity quarterly hour values of the water in the Atlas-Mansfield sewer at its confluence with the Welland River (25 March 1986, 12 noon to 12 midnight).
Table III	The commoner algae and microheterotrophs scraped from the mud (Zone 1) and *Phragmites communis* stems (Zones 2-5) near the outfall of the Atlas-Mansfield outfall.
Table IV	The commoner algae and microheterotrophs scraped from the mud (Zone 1) and *Typha latifolia* stems (Zones 2-5) near the confluence of Thompson's Creek and the Welland River.
Table V	Microbiotic species richness and Shannon-Weiner and Simpson diversity indices in each of the zones above and below the Cyanamid and the Atlas-Mansfield outfalls to the Welland River. The Shannon-Weiner diversity (Y) was regressed against the zone location number for each of the five zones (X axis) to provide the summary data set at the bottom of the table.

TABLE I (Cyanamid)

Time of Day	Conductivity	Time of Day	Conductivity
12 noon =	1,000 (μS/cm)	6:15 =	1,000 (μS/cm)
12:15	900	6:30	900
12:30	900	6:45	900
12:45	1,000	7:00	900
1:00	900	7:15	900
1:15	900	7:30	900
1:30	900	7:45	900
1:45	1,000	8:00	900
2:00	1,000	8:15	900
2:15	1,000	8:30	900
2:30	1,000	8:45	800
2:45	1,000	9:00	800
3:00	1,000	9:15	800
3:15	1,000	9:30	800
3:30	900	9:45	900
3:45	900	10:00	800
4:00	900	10:15	800
4:15	900	10:30	800
4:30	900	10:45	800
4:45	900	11:00	800
5:00	900	11:15	800
5:15	900	11:30	1,300
5:30	900	11:45	1,500
5:45	900	12:00 mid.	800
6:00	1,800		

Mean conductivity = 920 μS/cm for 49 samples. The 2 peaks in conductivity during the same period were 2,150 and 1,780 μS/cm.

TABLE II (Atlas Mansfield)

Time of Day	Conductivity	Time of Day	Conductivity
12 noon =	1,800 (μS/cm)	6:15 =	1,400 (μS/cm)
12:15	1,800	6:30	2,400
12:30	1,300	6:45	600
12:45	3,000	7:00	1,500
1:00	2,000	7:15	900
1:15	1,900	7:30	700
1:30	1,500	7:45	900
1:45	1,800	8:00	400
2:00	2,500	8:15	1,200
2:15	1,700	8:30	900
2:30	1,000	8:45	700
2:45	1,200	9:00	600
3:00	2,100	9:15	800
3:15	2,000	9:30	600
3:30	1,900	9:45	1,500
3:45	800	10:00	800
4:00	600	10:15	600
4:15	500	10:30	900
4:30	500	10:45	800
4:45	500	11:00	900
5:00	500	11:15	800
5:15	2,100	11:30	900
5:30	2,000	11:45	700
5:45	1,500	12:00 mid.	900
6:00	2,200		

Mean conductivity = 1,149 μS/cm for 49 samples. 7 peaks during this same period were 4,200, 4,500, 4,900, 5,000, 3,400, 4,000 & 3,00 μS/cm.

TABLE III

	Upstream of* Atlas-Mansfield Outfall Zone 5 200m	** Impact Zone Zone 1 0-20m	Primary* Recovery Zone Zone 2 20-200m	Secondary* Recovery Zone Zone 3 200-400m	Tertiary* Recovery Zone Zone 4 400m-1 km
CHLOROPHYTA					
FILAMENTOUS GREEN ALGAE					
Zygmena	1				1
NON-FILAMENTOUS GREEN ALGAE					
Ankistrodesmus falcatus	3		1	1	2
microflagellates	3		3	4	2
EUGLENOPHYTA					
Euglena convoluta				1	
BLUE GREEN ALGAE (CYANOPHYCEAE)					
Chroococcus sp.	2				1
Oscillatoria sp.	2			4	3
Spirulina cf Nordstedii	3				3
Rhabdoderma sp.	3				2
BACILLARIOPHYTA					
Achnanthes sp.	1		1	1	1
Cocconeis sp.	1				1
Fragilaria crotonensis				4	2
Gomphonema angustatum				3	3
Navicula sp.	2		2	1	2
Nitzschia palea		1	1	1	
Nitzschia sp.	2		1	2	1
Pinnularia sp.					1
Stauroneis smithii					1
Surirella sp.	1			2	1
CILIOPHORA					
Colpidium	1				
Opistotricha	1				
Tetrahymena	3				
Trinema cf compressum	1				
RHIZOPODA					
Colorless Rhizopoda <5	1		2	2	3
SARCODINA					
Colorless micro-flagellates <5	3	1	3	2	1

* Epiphytic taxa growing on Phragmites

** Epipelic taxa only

TABLE IV

Species Name	* Upstream of Cyanamid 200m	** Zone 1 impact zone 20m	** Zone 2 20-200m	** Zone 3 200-1,000m	** Zone 4 1-2 km
CHLOROPHYTA					
microflagellates (<5 µm)	3	1	2	3	3
FILAMENTOUS GREEN ALGAE					
Mougeotia sp.	2			1	2
Ulothrix sp.	2	1	1	1	2
EUGLENOPHYTA					
Euglena convoluta	1	4	2	2	1
BLUE-GREEN ALGAE (cyanophyceae)					
Oscillatoria sp.	2	2	2	2	1
BACILLARIOPHYTA					
Achnanthes sp.	1			1	1
Gomphonema sp.	1	2	2	1	1
Gyrosigma sp.				1	
Navicula sp.	3	3	3	3	2
Nitzschia sp. 1	2	2	2	3	2
Nitzschia palea	2	3	2	2	3
Nitzchia sp. 2	1			1	2
Pinnularia sp.	3		2	3	3
Stauroneis smithii	1				1
Surirella sp.	1			1	1
Tabellaria fenestrata	1				
PYRROPHYTA					
Glenodinium sp.	1	3		1	
CILIOPHORA					
Colpidium sp.		1	1		
Colpoda sp.		2	1	1	1
Opisthotricha sp.	1	1	2	2	2
RHIZOPODA					
Colorless amoebae	1	2	2		1
SARCODINA					
Monas	2	3	2	1	1
Colorless Monoflagellates <15 µm		1	1		1
BACTERIA					
Bacteria	1	3	3-4	1	1

* Epiphytic taxa growing on Typha

** Epipelic taxa only

TABLE V

	Cyanamid - Outfall			Atlas-Mansfield Outfall		
	Species Richness	Shannon Diversity	Simpson Diversity	Species Richness	Shannon Diversity	Simpson Diversity
Zone 1	16	1.6	0.48	2	1.0	0.53
Zone 2	16	1.8	0.54	8	1.4	0.56
Zone 3	19	2.3	0.73	14	1.9	0.69
Zone 4	20	2.3	0.74	18	2.5	0.79
Zone 5 (upstream station)	20	2.3	0.74	18	2.9	0.85

```
Summary data for:  X *       Y *

Sample Size (N):   5         5  ***
  Sums:           15        10.3
  Means:           3         2.06
  Sum of Squares: 10          .452
  Sum of Sq. YX:       1.9
  Variance Y on X:     .0303333333
  Slope:               .19
  S.E. of Slope:       .0550757054
  T for Slope=0(3 DF) 3.44979694
  Y-Intercept:         1.49
  Proportion of Y-Var
  due to X (R-squared) .798672567
  Bi-variate Normal
  Corr. Coefficient (R).893684825
```

```
Summary data for:  X **   Y **

Sample Size (N):   5      5   ***
  Sums:           15      9.7
  Means:           3      1.94
  Sum of Squares: 10      2.412
  Sum of Sq. YX:       4.90000001
  Variance Y on X:     3.66666579E-03
  Slope:                .49
  S.E. of Slope:        .0191485399
  T for Slope=0(3 DF)25.5894185
  Y-Intercept:          .47
  Proportion of Y-Var
  due to X (R-squared) .995439471
  Bi-variate Normal
  Corr. Coefficient (R).997717129
```

* where X = Cyanamid Zones 1-5 and Y = Shannon Diversity indices (Log base 2)

** where X = Atlas-Mansfield Zones 1-5 and Y = Shannon Diversity indices (Log base 2)

*** All diversity calculations were made on the basis of total biomass per taxon rather than total numbers per taxon.

Figure Captions

Figure 1 The Welland River study area detailing the location of zone 5 upstream of the Atlas-Mansfield outfall (No. 1) and Zones 1-4 (No. 2) downstream of the same as well as zone 5 upstream of the Cyanamid Chemical Company (No. 3) and zones 1-4 below the confluence of Thompson's Creek. The inset represents the location of the study area in the Niagara Peninsula.

Figure 2 Evidence of shock loading to Thompson's Creek (upper figure) and to the Atlas-Mansfield sewer (lower figure) based on continuous 24 hr specific conductivity data for these two locations.

Figure 3 Schematic representation of the higher aquatic plant zonation pattern above and below a toxic outfall.

Fig. 1

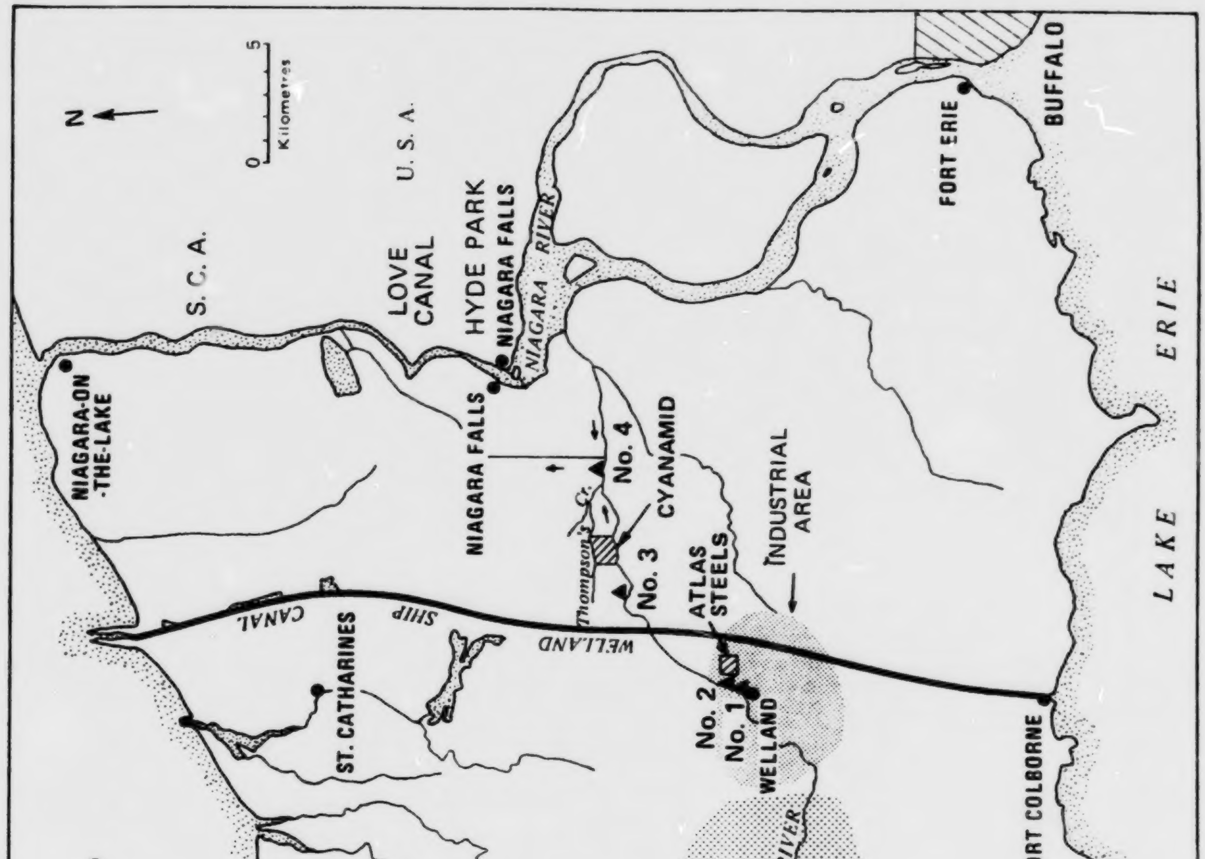
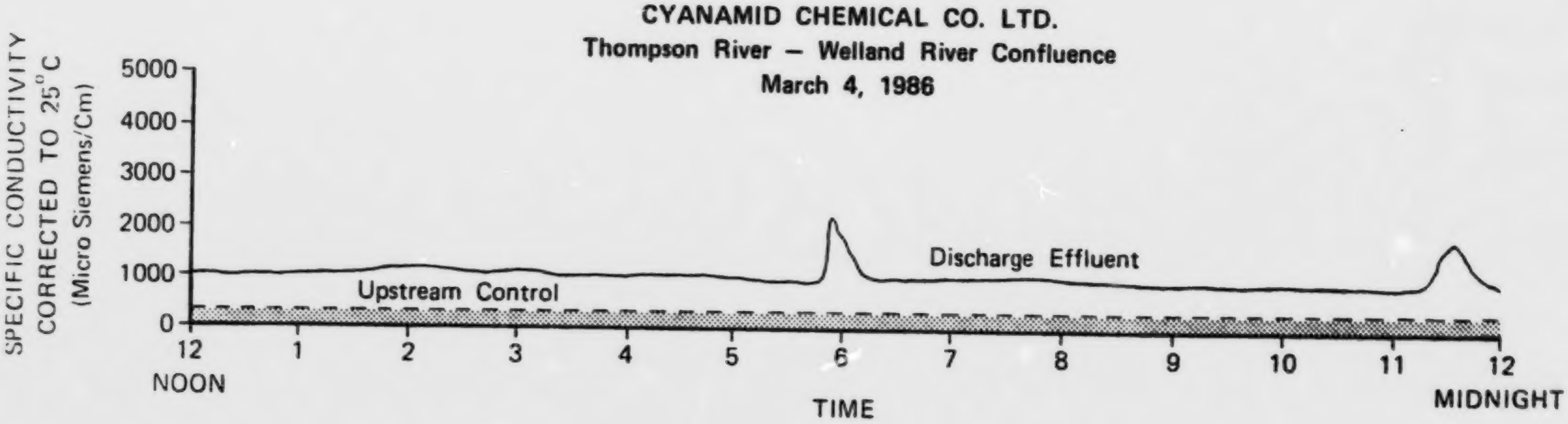
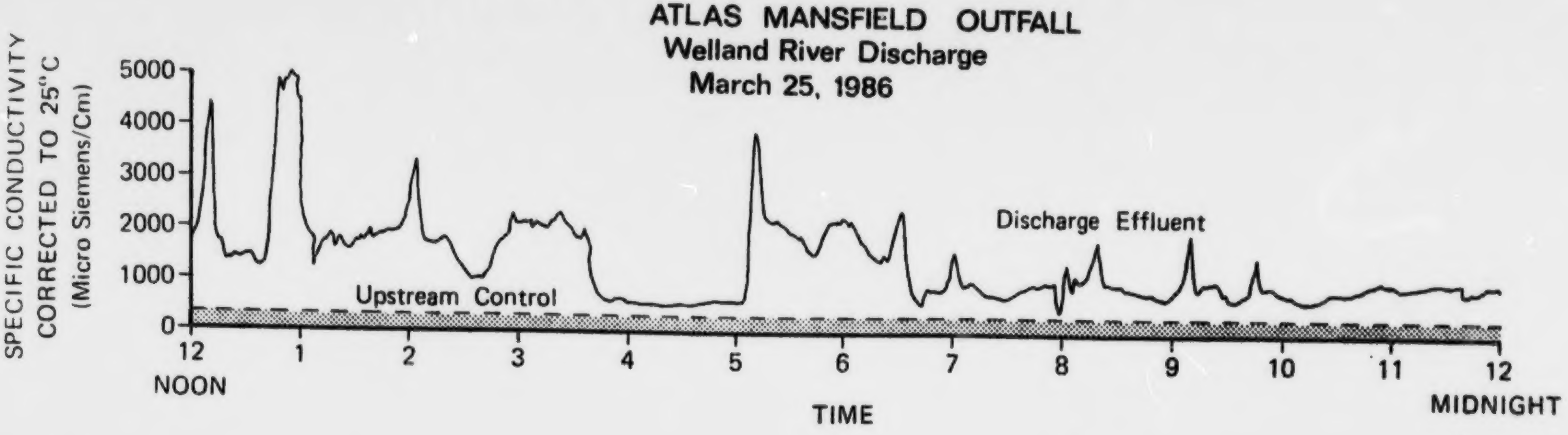

LAKE ONTARIO
NIAGARA-ON-THE-LAKE
S.C.A.
LOVE CANAL
HYDE PARK
NIAGARA FALLS
U.S.A.
N
0 5
Kilometres
NIAGARA RIVER
NIAGARA FALLS
FORT ERIE
BUFFALO
LAKE ERIE
PORT COLBORNE
WELLAND
No. 1
No. 2
ATLAS STEELS
INDUSTRIAL AREA
No. 3
CYANAMID
No. 4
Thompson's Cr.
WELLAND SHIP CANAL
ST. CATHARINES
WELLAND RIVER
AGRICULTURAL AREA
Lake Huron
Detroit
Lake Erie
Cleveland
Toronto
Hamilton
Lake Ontario
Buffalo

Fig. 2

CONTINUOUS CONDUCTIVITY SERIES



CYANAMID CHEMICAL CO. LTD.
Thompson River – Welland River Confluence
March 4, 1986

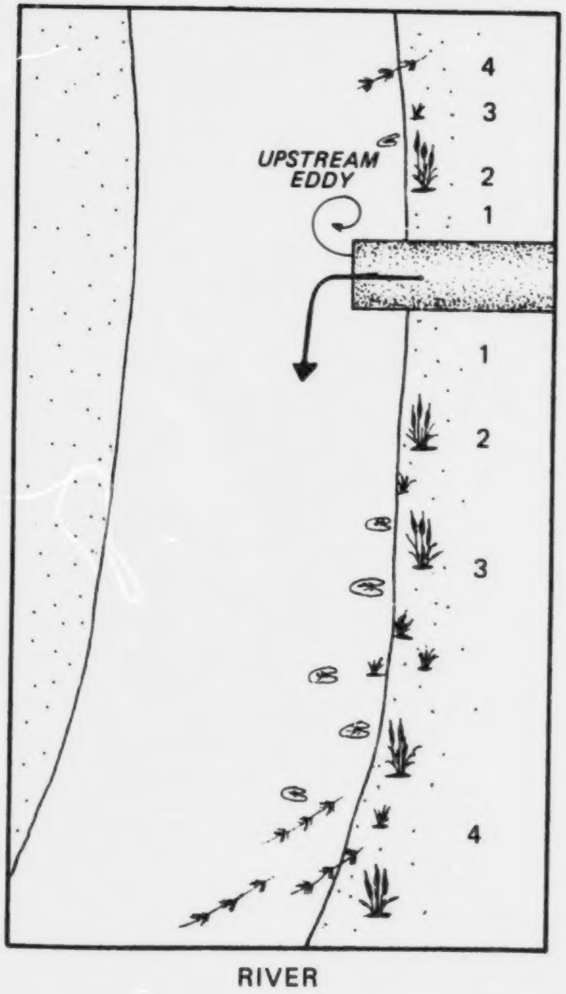


ATLAS MANSFIELD OUTFALL
Welland River Discharge
March 25, 1986

FIGURE 3 IDEALIZED ZONATION PATTERNS

KEY

1 IMPACT ZONE
2 PRIMARY RECOVERY ZONE
3 SECONDARY RECOVERY ZONE
4 TERTIARY RECOVERY ZONE


4
3
2
1
UPSTREAM EDDY
1
2
3
4
RIVER

EVALUATION OF CONTAMINANT VELOCITY IN LOW-PERMEABILITY FRACTURED SHALE

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Introduction

Knowledge regarding the subsurface migration of toxic contaminants from waste disposal or industrial sites in shale areas has become important in much of the heartland of the heavily-industrialized regions of southern Ontario. In the Oakville-Mississauga region, the Dundas shale is not far beneath ground surface. The Burlington-Hamilton region has the Queenston and Rochester shales and the Niagara Falls region has various shales including the Queenston shale at waste disposal and industrial sites; in the Niagara Falls region the Queenston shale lies beneath other rock units but it is an important hydrogeologic zone that may transmit contaminants through to the Niagara River.

One of the most important steps in the prediction of the extent to which groundwater contamination will occur at municipal landfills and at other waste disposal sites is the determination of the average velocity of non-reactive contaminant migration in groundwater. In our investigations of groundwater contamination, we have found that the greatest difficulties and uncertainties in contaminant velocity measurements and predictions occur at sites on fractured bedrock. For example, hydrogeologic investigations performed on the Queenston shale at Bayview Park landfill site have shown that this shale has a relatively low apparent hydraulic conductivity (i.e. low permeability) except at very shallow depth where weathering is an obvious cause of higher permeability. This finding of generally low permeability is consistent with previous studies of this shale in the Burlington-Hamilton area. Our investigations of the Bayview Park site have also shown, although not in an entirely conclusive manner, that the velocity of migration of non-reactive contaminants in this low-permeability shale is relatively large. This leads to the expectation that very large contaminant plumes can develop in fractured shale under conditions of relatively low contaminant mass flux through the shale.

If our preliminary finding of relatively large horizontal contaminant velocities in the Queenston shale is correct, it is reasonable to expect that landfills situated on fractured shale can produce large plumes of groundwater contamination that extend over considerable distances from the contaminant source. Our objectives, therefore, are (i) to apply and evaluate various methods for velocity determination in low-permeability zones in the shale, (ii) to determine whether or not our preliminary finding of large horizontal contaminant velocity in the shale is correct, and (iii) to assess the degree to which diffusion of contaminants from the fractures in the porous rock matrix can attenuate rapid advection along the fractures.

Study Site

A site on Petro-Canada property in Clarkson, Ontario was selected and a preliminary phase of drilling and instrumentation has been performed. The site was chosen for several reasons. It is located on the Dundas shale, a moderate- to low-permeability fractured shale hydrogeologically similar to other shale deposits in Southern Ontario. General background hydrogeological information was available indicating a shallow water table, thin overburden (2 metres), and flay lying bedrock. The site has easy access and is a secure site with respect to long-term monitoring and limited potential for vandalism.

A preliminary drilling program conducted in May, 1986 utilized a track mounted CME750 drill rig from the University of Waterloo. Five boreholes were continuously cored using an NV3 core barrel. The boreholes were placed 15 metres apart in two perpendicular rows of three.

Each borehole was drilled in the following manner. Hollow stem augers were advanced until refusal in the weathered bedrock at approximately 3 metres depth. The borehole was then drilled by triconing to a depth of approximately 5.5 metres. This was done because the upper weathered bedrock had a number of clay zones causing problems with water circulation during coring of the first borehole. Boreholes were cored from approximately 5.5 metres to 16.5 metres below ground surface at each location.

Results of rock coring indicate that the majority of the rock is a shale with some layers of dolomite within the shale. The dolomite zones are generally 5-20 cm thick. The fracture pattern is primarily horizontal in the shale and vertical in the dolomite. Many of the dolomite zones had broken shale above and below; however, it was difficult to determine if this was induced by drilling.

The degree of fracturing generally decreased with depth as the RQD ranged from 50% in the upper bedrock to 80-85% in the lower part of the borehole. Fractures were generally along bedding planes and were usually tight. Some vertical fractures in the dolomite had precipitation of either marcasite or pyrite indicating water movement through these fractures.

The rock core was logged in the field and photographed in 60 cm sections. Several fracture zones were encountered during drilling of each borehole. The location of these main fracture zones were correlated between each borehole using the field logs and photographs of the core to determine which fracture zones could be continuous across the site. The main fracture zones encountered which showed the potential for continuity across the site were at depths 6.5-6.8 metres, 7.2-7.6 metres, 10.4-10.7 metres and 14.0-14.3 metres below ground. Many of these zones contained dolomite beds.

Instrumentation and Hydraulic Response Tests

Once the drilling was completed, casing was installed in the upper 5 metres of the borehole and the borehole left open to allow for downhole testing. The first testing conducted was pressure-packer permeability testing of the main fracture zones encountered to estimate the permeability of these zones and also determine if the fracture zones were very localized.

The fracture zones were isolated using a double packer assembly which was pneumatically inflated with nitrogen. Water was then injected into the isolated zone at a constant pressure and flow rate. The water was injected from a series of interconnected reservoirs of various diameters (1.25 cm - 6.5 cm) to allow for better calibration at low flow rates (i.e. if the test zone was tight than a small diameter reservoir was used and if the test zone was quite permeable than all the reservoirs were used).

General results of packer testing indicated that the zone of highest permeability (on the order of 5×10^{-4} to 1×10^{-4} cm/s) is located at depths between 10.4-10.7 metres. Because the actual zone tested was 1.2 metres in length, this range in hydraulic conductivity values can only be regarded as a bulk estimate for the fracture zone. Additional testing of a more localized nature (smaller test intervals) is being performed to determine if this zone is suitable for a natural-gradient tracer test to directly assess contaminant flux rates.

Other zones tested had a lower permeability, but many of these tests exhibited a decrease in a rate of flow of injected water as the test continued. This decrease occurred for each increase in injection pressure and would appear to indicate that many of these fracture zones were localized and not continuous in lateral extent. In this case, the permeability of the matrix becomes the controlling factor for water movement. The rock zone above and below the most permeable fracture zone (10.4-10.7 metres below ground) was packer tested in several of the boreholes and the permeability was estimated to be less than 10^{-7} cm/sec.

Several double-packer systems were constructed to isolate the main fracture zone at two boreholes with the standard pressure packer system being used at a third borehole to isolate and pump the main fracture zone. A short-term pumping test was then performed to determine if this fracture zone is well connected and if so, aid in the design of a long-term pumping test utilizing a multilevel packer system situated in all boreholes.

Results of the short term pumping test indicate that a hydraulic connection exists between at least four of the five observation wells. The test zone was pumped at approximately 1.5 L/min.

A multilevel double-packer system has been constructed and installed in each borehole to isolate discrete zones for detailed response testing and to allow routine water-level monitoring within each zone. Up to five discrete zones can be isolated with this packer system. The system contains a series of packers which are inflated pneumatically and have holes drilled and threaded through the upper and lower bulkheads of each to connect tubing from each zone up to ground surface. The length of each of the five test intervals can be varied with this monitoring device as well as the depth of placement.

Use of the multilevel monitoring devices permit estimation of detailed permeability profiles by single-well hydraulic responses and borehole dilution testing. In addition, such devices allow determination of the degree of fracture interconnectivity between boreholes when one of the zones is pumped continuously. Work of this nature is currently in progress.

Velocity Determination

The following methods are being implemented to estimate the groundwater velocity in the fractured shale at the test site.

1. calculations based on Darcy's law and measured values of hydraulic conductivity, hydraulic gradient and estimates of effective fracture porosity
2. the borehole dilution test method (i.e. a single-borehole tracer test method)
3. natural-gradient and forced advection tracer tests (i.e. tracer tests using many multilevel devices for tracer monitoring).

Darcy's law for velocity determination is expressed as:

$$\bar{v} = Ki/n \tag{1}$$

where $\bar{v}$ is the bulk average linear groundwater velocity, K is the bulk hydraulic conductivity of the fractured rock, i is the hydraulic gradient, and n is the fracture porosity of the rock. In most types of fractured sedimentary rock in southern Ontario, n is expected to be somewhere in the range of about 0.01 to 0.00001, expressed as a fraction of the bulk rock unit volume. Thus, from Eq. 1, it is evident that even in rock with a low K value, the velocity may be large when the fracture porosity is small under conditions of moderate i values.

The main difficulty in the use of Eq. 1 for a bulk-average velocity lies in the determination of values of n. Well-accepted conventional methods can be used to determine values for K and i but there are no generally-accepted methods for determining values of n. Several methods are being investigated to determine apparent values of n so that the efficiency and accuracy of these methods can be evaluated. These methods include: pumping tests for water-table drawdown cone evaluation of n, calculation using the Snow equations based on the core description of fracture aperture and frequency, and natural and induced-gradient tracer tests.

The borehole dilution method provides a direct measure of the localized velocity rather than its indirect determination by means of Eq. 1. The test involves first isolating a test interval by means of packers and then monitoring the time-rate-of-change of a suitable tracer contained within the packed-off interval. From the concentration history measured in the packed-off interval, a simple mass balance equation allows calculation of the Darcy flux of groundwater flowing through the monitored interval. Because the shale is rich in sodium chloride, a dilute water can be used as the tracer with electrical conductance being the parameter monitored. By borehole-dilution testing at numerous depth intervals, velocity profiles so obtained can be compared to velocity profiles obtained on the bases of Eq. 1 using the independently-estimated permeability profiles obtained from the detailed hydraulic response tests as input.

An important factor not recognized by Eq. 1 is the effect of molecular diffusion of a contaminant from the fractures to the porous rock matrix. This diffusive exchange produced an "apparent" solute velocity in the fractures which is generally less than a groundwater velocity calculated on the bases of Eq. 1. Hence matrix diffusion can be regarded as an attenuation mechanism that reduces the solute flux along the primary paths of contaminant migration.

In order to investigate the potential for matrix diffusion as an attenuation mechanism in fractured shale, a natural-gradient tracer test is planned for the 1987 field season. Both a bromide and a trace amount of halogenated hydrocarbon such as trichloroethylene or dichlorobenzene will be used as tracers. It is desired to use at least two tracers with different diffusion coefficients in order to identify any differences in matrix diffusion effects that may occur. Additional multilevel devices will be installed in order to measure tracer arrival-time curves at various depths and areal locations. From these data, effective velocities can be ascertained. The depth interval having the largest connected hydraulic conductivity will be selected for tracer injection. A variety of mathematical models developed at the University of Waterloo for the problem of advective-diffusive in fractured rock can be applied to the experimental results to determine their ability to predict contaminant advance rates in such geologic settings.

Concluding Remarks

The concern regarding contaminant migration in shale relates to the possibility for contaminants from waste disposal sites or hazardous liquid spills to migrate in groundwater through the shale to locations where they can enter surface water bodies or water supply wells located in underlying aquifers. The manner in which contaminant velocities are currently predicted in shale is close to guess-work. We expect that our investigation of methods of velocity determination will provide an improved basis for consultants and government agencies to determine velocities during investigations of sites on shale.

GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS

Part 2: Laboratory investigation of strength and mineralogy

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1.0 Introduction

The surficial overburden of Southwestern Ontario is dominated by extensive deposits of clays and clay tills which were formed within large glacial lakes or underneath thick glaciers during the Wisconsin glaciation. These fine-grained sediments are very susceptible to changes in structure and mineralogy when exposed to surface weathering, as they are in large parts of Southwestren Ontario. These physical and chemical alterations may persist to depths in excess of 10 meters depending on the type and intensity of weathering. Soderman, Kenney and Loh (1961) reported a hard to stiff crust extending to depths as great as 40 feet (12 m.) in the Lake St. Clair region of Ontario; Lo, Adams and Seychuk (1969) reported that the Nanticoke site on the north shore of Lake Erie was underlain by 20 to 35 feet (6 to 10.7 m.) of heavily dessicated and fissured clay; Quigley and Ogunbadejo (1976) presented profiles of the Sarnia clay tills which placed the depth of the weathered crust at approximately 5 meters. The physical consequences of weathering reveal themselves as changes in strength, compressibility and permeability with respect to the underlying, unweathered sediments of the same geological unit. The chemical alterations reveal themselves through leaching and precipitation of carbonates and hydroxides as well as through changes in clay mineralogy.

The objective of this particular study has been two-fold : 1) to examine, on a site-specific basis, the macrofabric of the surface clays and clay tills; 2) to determine the degree of alteration of geomechanical parameters and mineralogy along the weathered/unweathered profile of each site. In addition, a regional investigation was undertaken to obtain results that may reflect the role of different geologic and geomorphologic characteristics in producing the surface weathered zones of Southwestern Ontario.

The following three sites were chosen for the investigation: 1) the Nanticoke site located in the varved lacustrine Haldimand clays along the north shore of Lake Erie, 2) the London site located on Port Stanley till south of the City of London, 3) the Essex site located on the "water-laid" tills of the St. Clair clay plains region (Figure 1). A discussion of the geology of each site as well as the results of the first objective have been published in Part I of this study (Dusseault and Vorauer, 1985). The purpose of this paper is to report the results of the laboratory investigations undertaken during 1986, making use of large diameter Shelby tube samples collected during the field component of this study.

2.0 Results of the geomechanical testing

At each of the three sites mentionned in the preceding section, two vertical boreholes were augered using 6-inch (15.2

cm.) diameter solid stem augers. At 5-ft intervals (1.5 m.), the auger string was removed and a 4.25-inch (10.8 cm.) ID Shelby tube lowered into the hole and hydraulically driven into the soil 24 inches (61 cm.). Since the objective was to obtain samples of the weathered and unweathered zones only, the London and Essex deposits were sampled to 12 m. and the Nanticoke deposit only to 9.15 m. where bedrock was encountered. Each tube was sealed in microcrystalline wax and transported to the laboratory where the samples were extruded, sectionned and waxed for storage. Numerous fractures were visible in the upper 3 to 4.5 m. in the London and Essex deposits and down to 9.15 m. in the Nanticoke deposits. The fractures were identified by a light grey infilling material and a discolouration zone 1 to 1.5 cm thick on either side. Extensive root systems were also visible along the fracture planes especially at Nanticoke. Dark streaks, possibly manganese oxides, were common along the fracture planes of the Essex samples.

2.1 Atterberg limits and natural water contents

For each site, a depth profile showing variations in the natural water contents, plastic limits and liquid limits is presented in Figure 2. The classic profile of a weathered crust is represented in all three cases, where the natural water contents near the surface ie top 3.5 to 4.0 m., are below the plastic limits of the soils. A feature which is common to the London and Essex tills is that the water contents are very close to the plastic limits (18-21). This is an initial indication of the behaviour of the soils which possess the characteristics of both semi-solids and plastic solids. Their generalized stress-strain curves would show a quick mobilization of the peak strength at small strains followed by a gradual loss in strength at larger strains. The liquid limits range between 32 and 36 and in both cases do not vary significantly with depth. The Nanticoke lacustrine clays are more plastic than the tills and exhibit higher plastic and liquid limits. The anomalously low Atterberg limits at 6 m. are believed to be testing errors and not indicative of inherent variations within the varved deposits.

The Casagrande plasticity chart shown in Figure 2 represents clearly the plasticity groupings aforementionned. The data points plotting above the A-line indicate that the fines fraction of all three soils is dominated by inorganic clays. A simple identification of the dominant clay minereal in the soils can be made using the plasticity chart published in Holtz and Kovacs (1981, p.89). The Atterberg limit data plotting just above the A-line is representative of illitic clays.

It most be stated that the water content profiles of Figure 2 are not, on their own, indicative of the ultimate depth of desiccation but rather represent a minimum depth.

2.2 Oedometer consolidation tests

The purpose of this series of tests was to determine the overconsolidation ratio (OCR) associated with the weathered/unweathered profiles at all three sites. The results of the testing are shown in Figure 3 as plots of void ratio versus logarithm of effective stress. One of the obvious characteristics of all of the curves shown is the absence of any distinctive break in their slope as is generally expected once the preconsolidation pressure has been exceeded. The gentle curvature of the e-log effective stress plots has been associated with weathered clays in the upper crust by Bjerrum (1973). These plots are representative of a reduced compressibility compared with that of the unweatherd clay, due to formation of aluminium and iron hydroxides acting as weak cement. Sample disturbance is another factor which may affect the void ratio-effective stress behaviour as shown by Schmertmann (1955). Schmertmann developed a procedure for testing overconsolidated clays taking into account sample disturbance. His procedure includes a cycle of partial unloading and reloading starting at the approximate preconsolidation pressure. This procedure has also been recommended by Leonards (1976) to attempt to reproduce as closely as possible the in-situ stress state ie geological unloading from the maximum overburden pressure.

Table 1 shows the results obtained from the Schmertmann procedure:

	Depth (m.)	OCR	Cc	Cr
London #3	4.57	4.08	0.178	0.019
London #12	6.10	3.45	0.165	0.028
London #13	7.62	1.55	0.182	0.027
London #15	10.70	2.19	0.222	0.024
Essex #1	1.37	8.52	0.142	0.032
Essex #2	3.05	3.35	0.140	0.030
Essex #3	4.57	5.62	0.244	0.030
Essex #4	6.09	5.00	0.251	0.024
Essex #6	9.15	1.90	0.215	0.028
Nanticoke #1	1.52	8.10	0.220	0.040
Nanticoke #2	3.05	5.90	0.315	0.043
Nanticoke #3	4.57	3.10	0.332	0.053
Nanticoke #4	6.10	2.10	0.343	0.048
Nanticoke #5	7.62	1.09	0.405	0.043

OCR = preconsolidation pressure/existing overburden pressure
Cc = compression index
Cr = recompression index

There are several mechanisms which have acted upon the clays and clay tills of Southwestern Ontario to produce the overconsolidation observed in the oedometer tests. The London site has been subjected to a change in total stress produced by deglaciation followed by chemical alteration and desiccation due to surface drying. The near surface samples proved to be so brittle that placement of the consolidation ring lead to large disturbances of the samples. The increase in OCR at 10 m. may reflect a sample obtained from the underlying Westminster Moraine which was overidden during the deposition of the Port Stanley till. The Essex site located in the "water-laid" tills near Lake St. Clair was probably subjected to a change in pore pressure due to groundwater lowering which accompanied a general lowering of lake levels between 12,000 and 8,000 years B.P. (Soderman and Kim, 1970). This was then followed by desiccation and chemical weathering at the near surface producing large apparent OCR's. The Nanticoke site has also been subjected to changes in pore pressure due to groundwater lowering but not to the same degree as the Essex site, as evidenced by comparatively lower OCR's. The higher void ratios at the Nanticoke site (Figure 3) are due to the lacustrine origin of this deposit.

The compression indices from all three sites show a generally increasing trend with depth indicating that there has been lesser structural alteration. The recompression indices appear to be independent of depth and OCR and they are not parallel to the final rebound curves.

2.3 Laboratory hydraulic fracture tests

An investigation into the tensile strength of the weathered and unweathered clays was undertaken as this parameter may have a controlling influence upon the behaviour of the fractured and non-fractured material subjected to tensile stresses. These stresses can develop at the bottom of large excavations such as those constructed for the disposal of liquid and solid wastes. Soil rupture or fracture reopening could prove detrimental to the integrity of such waste disposal facilities.

A laboratory hydraulic fracture test was developed by Decker and Clemence (1981) to study the hydraulic fracture initiation in compacted soils. They determined that a series of hydraulic fracture tests could be used to calculate an acceptable value for the tensile strength of the soil. The test involved inserting a small diameter needle with radial outlet ports into the middle of a compacted soil of low plasticity. The soil would then be consolidated under an appropriate effective cell pressure until complete consolidation was attained. Fracturing of the sample would then be accomplished by uniformly increasing the fluid pressure within the injection needle, until an abrupt increase in flowrate occurred indicating failure of the sample. A series of three to four of this tests would be completed using different samples consolidated under higher confining pressures. The analysis then involved plotting the data on a confining pressure versus failure pressure plot and drawing a straight line through the points. The failure pressure at zero confining pressure was taken as the tensile strength of the soil. A variation on this type of laboratory method was also attempted by Bjerrum and Andersen (1972) in studying the measurement of lateral earth pressures. They stated that the critical water pressure at which permeability increased abruptly was related to the effective stresses around a piezometer tip as well as the tensile strength of the soil.

In the present study, 4-inch (10 cm.) diameter and 8-inch (20 cm.) long samples of undisturbed clay were tested. Fluorescein dye was added to the injection fluid as recommended by Bjerrum and Andersen (1972) since they observed that without a tracer, the induced fracture would not have been visible upon sectionning of the sample. This may have been due to the reconsolidation of the clay following pressure relief.

The results of the hydraulic fracture tests are presented in Figure 4 as a plot of confining pressure versus rupture pressure, along with the data presented by Decker and Clemence (1981) for compacted low plasticity soil. In general, the results for the undisturbed clays plot at much higher rupture pressures than for the compacted soils. Samples tested more than once show a trend of rupture pressures less than those tested only once at any given confining pressure. This may be due to a remoulding of the soil along the induced flow path within the sample. Some of the intact and fractured samples do plot along a linear trend who's regression provides an abscissa intercept at 51 kPa (r = 0.894). However, the significance of this tensile strength value remains unclear as both weathered and unweathered, and intact and fractured samples were tested. Following the early tests on intact clays, no fluorescein could be detected under ultra-violet light. The concentration of the tracer was subsequently increased for the tests on fractured samples, which then allowed visual confirmation of induced flow paths along fracture planes adjacent to the probe outlets.

Ingles (1962) has stated that high capillary stresses will develop in a partially saturated soil due to the formation of capillary menisci between particles. The results of his analysis lead to an empirical equation that relates tensile strength in kPa to a/d where a is in the range of 250 to 650 and d is the particle diameter in mm.. In fact, capillary stresses would be more directly related to the pore sizes in the soil which indicates that tensile strength may be dependent on soil structure, and in the case of clays also related to the effective confining pressures. It seems reasonable to suggest than, that at lower void ratios a partially saturated soil may exhibit greater tensile strength. This may help to explain the apparent increase in the tensile strength component of the rupture pressure with increasing confining pressure.

2.4 Consolidated-undrained triaxial tests

The objective of this series of tests was to examine any differences in stress-strain behaviour and strength between the weathered and unweathered zones at all three sites. To maintain sample homogeneity and to eliminate the time needed for sample preparation, the multi-stage triaxial testing method was used (Bishop and Henkel, 1972). This method requires only one sample to adequately define the shear strength envelope. It involves consolidating a sample at a particular effective cell pressure followed by slow shearing until just before failure. The same sample is then unloaded and reconsolidated at a higher effective cell pressure which is then followed by shearing again. Three tests at different effective cell pressures are usually required to determine the shear strength parameters.

The 10 cm. diameter by 20 cm. long samples were used for the triaxial testing to reduce the effect of sample size on shear strength. All samples were consolidated isotropically before shearing and a minimum saturation back-pressure of 207 kPa was used to dissolve any air in the sample and in the water lines (Bishop and Henkel, 1972). Skempton's B-parameter (change in pore pressure/change in cell pressure) was determined before each test and ranged between 0.85 and 0.96. For stiff soils, these B-values correspond to saturations greater than 96% (Black and Lee, 1973).

For the multi-stage tests, it was assumed that failure had occurred at maximum deviator stress. The strain-rate for all tests was 0.0012 inches/min. or 0.9%/hr.

The results from all CIU triaxial tests are presented in Figures 5 to 10 in terms of plots of shear stress versus strain, change in pore pressure versus strain and Q versus P. In all six cases, the soils show an overconsolidated behaviour which is exemplified by a decreasing pore pressure as peak shear strength is approached. This is associated with the phenomenon of dilation which is commonly observed in dense sands and overconsolidated clays. The fact that the change in pore pressure does not become negative indicates that these deposits are not heavily overconsolidated such as the England clays. The stress path plots (Q vs. P) are also indicative of overconsolidated soils and the maximum confining pressures of 207 and 240 kPa do not seem to have brought the soils into their normally consolidated state.

The secant moduli, taken at 50% of peak strength, is a function of confining pressure and sample depth, with higher elastic moduli being associated with the surface weathered crust. In general, the magnitude of the moduli are related in the following manner: Essex > London > Nanticoke. Since the elastic modulus is very sensitive to sample disturbance it is not surprising that the London moduli are smaller than the Essex moduli since they were much more difficult to sample using the Shelby tubes. This may be supported by the fact that the peak shear strengths of the London samples are higher than those from Essex. The following table summarizes the shear strength parameters developed from the stress path plots:

Table II

	C '(kPa)	PHI '
Nanticoke #1-1	13	36
Nanticoke #1-5	50	15
London #1	38	31
London #16	12	34
Essex #2	47	31
Essex #13	41	23

The Nanticoke surface sample shows the results of shear behaviour dominated by the movement of soil blocks along fissure planes. The confining pressures were not high enough to begin mobilizing the cohesion of the clay matrix material such as in the deeper sample showing high cohesion and low angle of friction. This phenomenon has also been reported by Baracos et al (1980) in their study of the Winnipeg lacustrine clays. The high cohesion and angle of friction values associated with the London and Essex samples is a reflection of their overconsolidated nature and till structure.

3.0 Clay mineralogy

The objective of the mineralogical analysis was to examine the results of weathering on the bulk clay mineralogy and also any differences in mineralogy between the weathered clay matrix and the coatings along the fracture plains. The X-ray diffraction technique was used for this purposes along with three samples from each of the study sites: one from the near-surface, another containing obvious infilled fracture planes and another from the unweathered zone at depth. Each sample was pre-treated for excess carbonate removal by mixing with a solution of sodium acetate and acetic acid. The less than 2 micron fraction was obtained using a standard sedimentation process and a small portion of the soil/water mixture was aloud to settle onto circular glass lenses. The following five treatments were performed preceding X-ray diffraction analysis at the University of Guelph facilities: 1) Mg - saturated, 2) Mg - saturated, glycol solvated, 3) K - saturated, air-dry, 4) K - saturated, heated to 500 C for 1 hr., 5) boiling in concentrated HCl for 15 minutes.

The following is a descriptive analysis of the results obtained. All of the samples showed basically the same trends, the clay minerals being dominated by the presence of illite with minor amounts of Fe-chlorite. Small amounts of vermiculite were also present in most samples, identified by a reduction of the 14 A peak and an intensification of the 10 A peak upon K saturation (Soderman and Quigley, 1965). Traces of kaolinite were also present in the Essex and Nanticoke clays evidenced by 7 A peak remaining after the HCl treatment. Interstratified minerals such as illite-chlorite were present in the London samples, as a persistant 8.4 A peak throughout the treatment process (Soderman and Quigley, 1965). No obvious amounts of smectite were detected in any of the samples although a decrease in Fe-chlorite peaks was noted in the near-surface samples from Essex and London. Quigley and Ogunbadejo (1973) noted this phenomenon in the Sarnia clay tills and correlated it with iron oxidation leading to swelling clay formation. Any swelling minerals in the samples tested for this study may only be present as interstratified clays such as illite-smectite or vermiculite-smectite evidenced by high backgrounds and short peaks in the low angle range ie greater than 24 degrees, (Mitchell, 1976). The fact that the samples were allowed to air-dry onto the glass lenses may have collapsed the smectite minerals permanently, not allowing re-swelling upon glycolation.

4.0 Conclusions

This study has examined the consolidation, strength and mineralogical characteristics of the weathered/unweathered profiles at three geologically different sites across Southwestern Ontario. The clays at all three sites have proven to be overconsolidated down to depths of at least 12 m. with the till deposits showing the largest degree of overconsolidation. Shear strength anisotropy does exist between the weathered and unweathered clays with the greatest difference occuring at the Nanticoke site. A laboratory tensile strength method has been attempted with the clay samples, however results are largely inconclusive at this point because direct testing of fractures within the samples proved difficult. This strength parameter should be given more attention especially in terms of constructing deep excavations for waste disposal. Silvestri and Tabib (1983) used a theoretical procedure to determine gravity stresses in finite elastic slopes. From their contoured diagrams of normalized stresses, it is evident that significant tensile stresses can develop at the base of excavations with the deepest zone of negative horizontal stress being associated with high angle, non-vertical slopes. For example, a 10 m. deep excavation with 60 degree slope in a material with unit weight of 20 kN/m3 and Ko=0.5 will have a tensile stress of 100 kPa generated at the base. Large amounts of swelling clays have not been detected in the near-surface matrix and fracture samples examined in this study. Vermiculite, which has a certain swelling potential, has been identified in small amounts in several near-surface samples. More detailed study of the mineralogy and potential tensile strength of the near-surface clays in Southwestern Ontario is required before an adequate understanding of the behaviour of fractured clays can be attained on a regional basis. The constant need to develop waste management facilities in less geologically favourable environments, underlain by thinner fine-grained units, will require a clearer understanding of this most difficult construction material.

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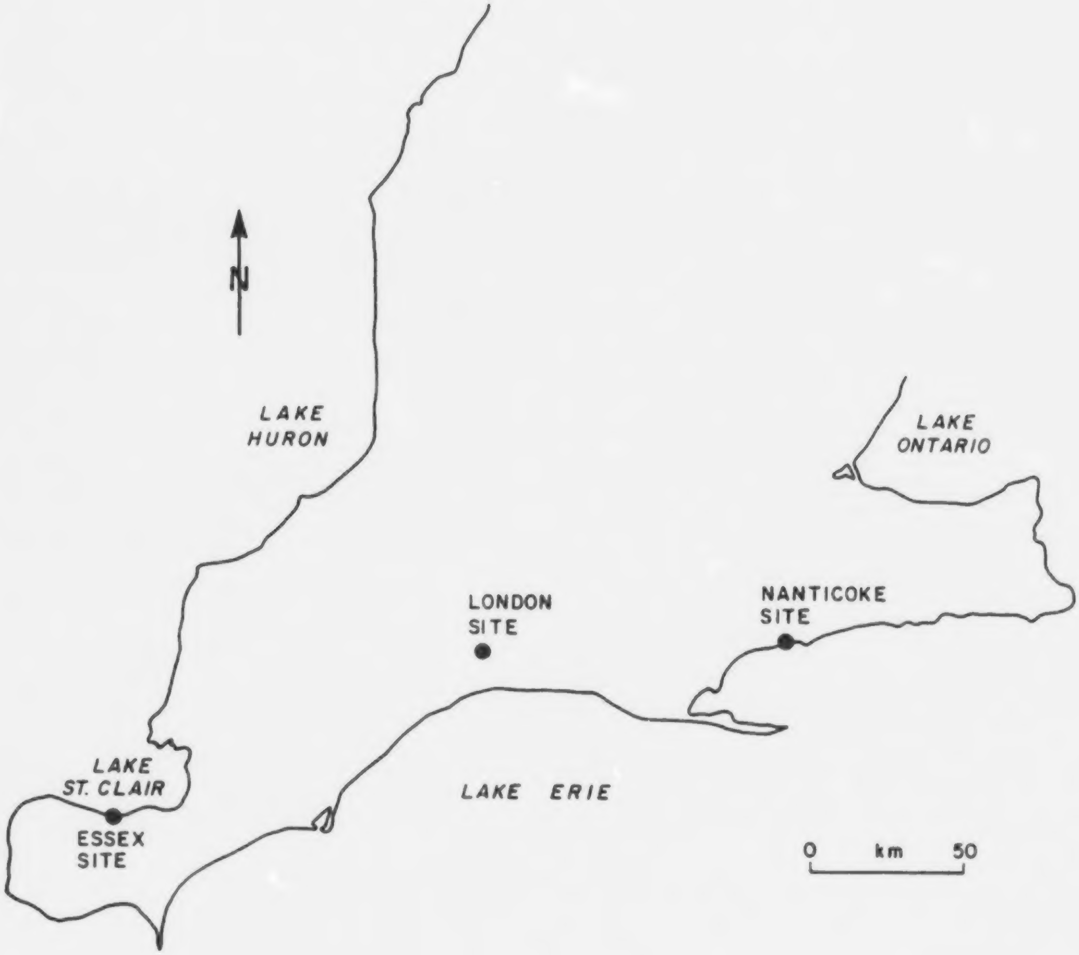

N
LAKE HURON
LAKE ONTARIO
LONDON SITE
NANTICOKE SITE
LAKE ST. CLAIR
ESSEX SITE
LAKE ERIE
0 km 50

Fiqure #1

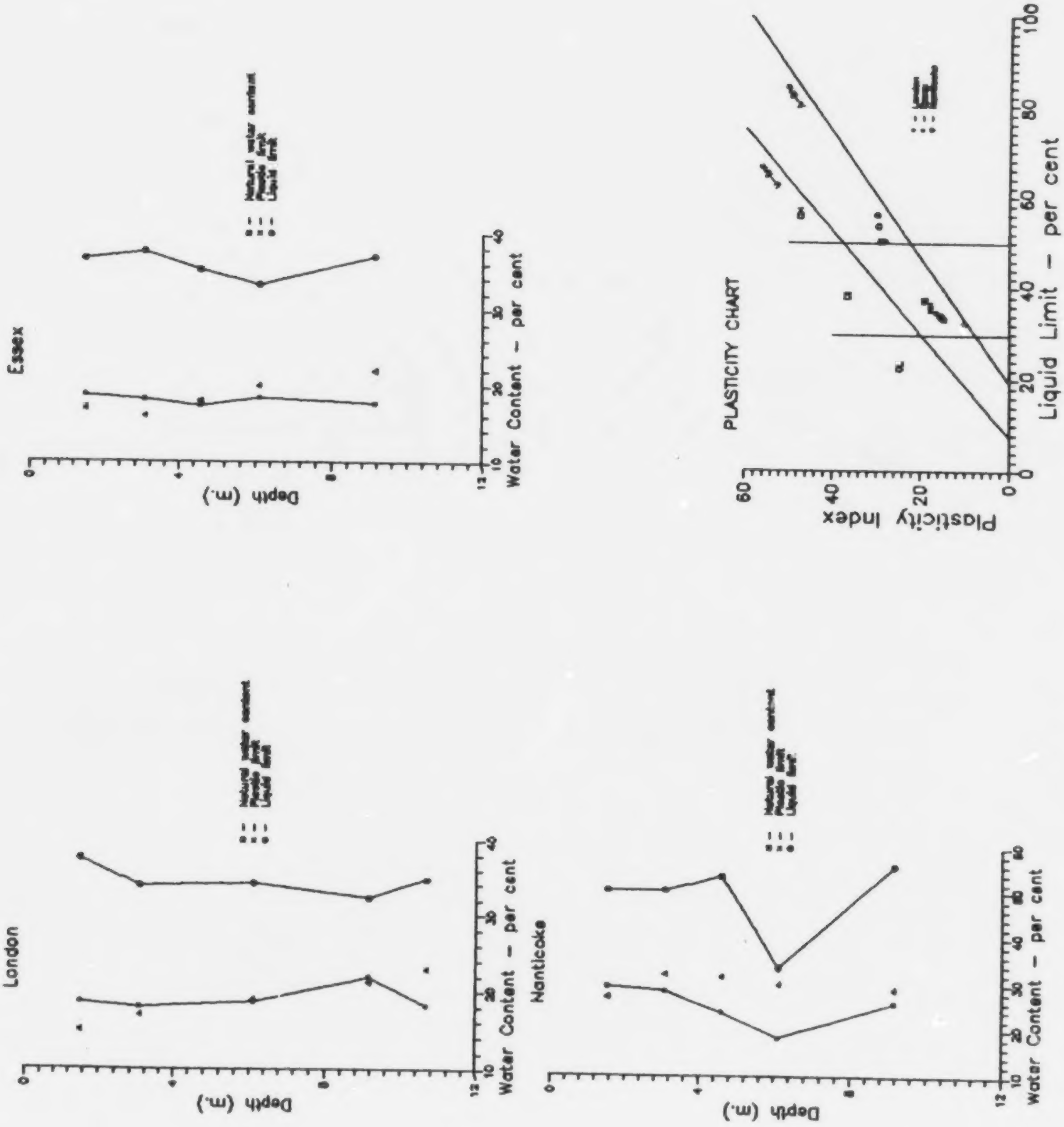

Essex
Depth (m.)
0
4
8
12
10
20
30
40
Water Content - per cent
Natural water content
Plastic limit
Liquid limit
PLASTICITY CHART
Plasticity Index
0
20
40
60
Liquid Limit - per cent
0
20
40
60
80
100
London
Depth (m.)
Water Content - per cent
Natural water content
Plastic limit
Liquid limit
Nanticoke
Depth (m.)
Water Content - per cent
Natural water content
Plastic limit
Liquid limit

Figure #2

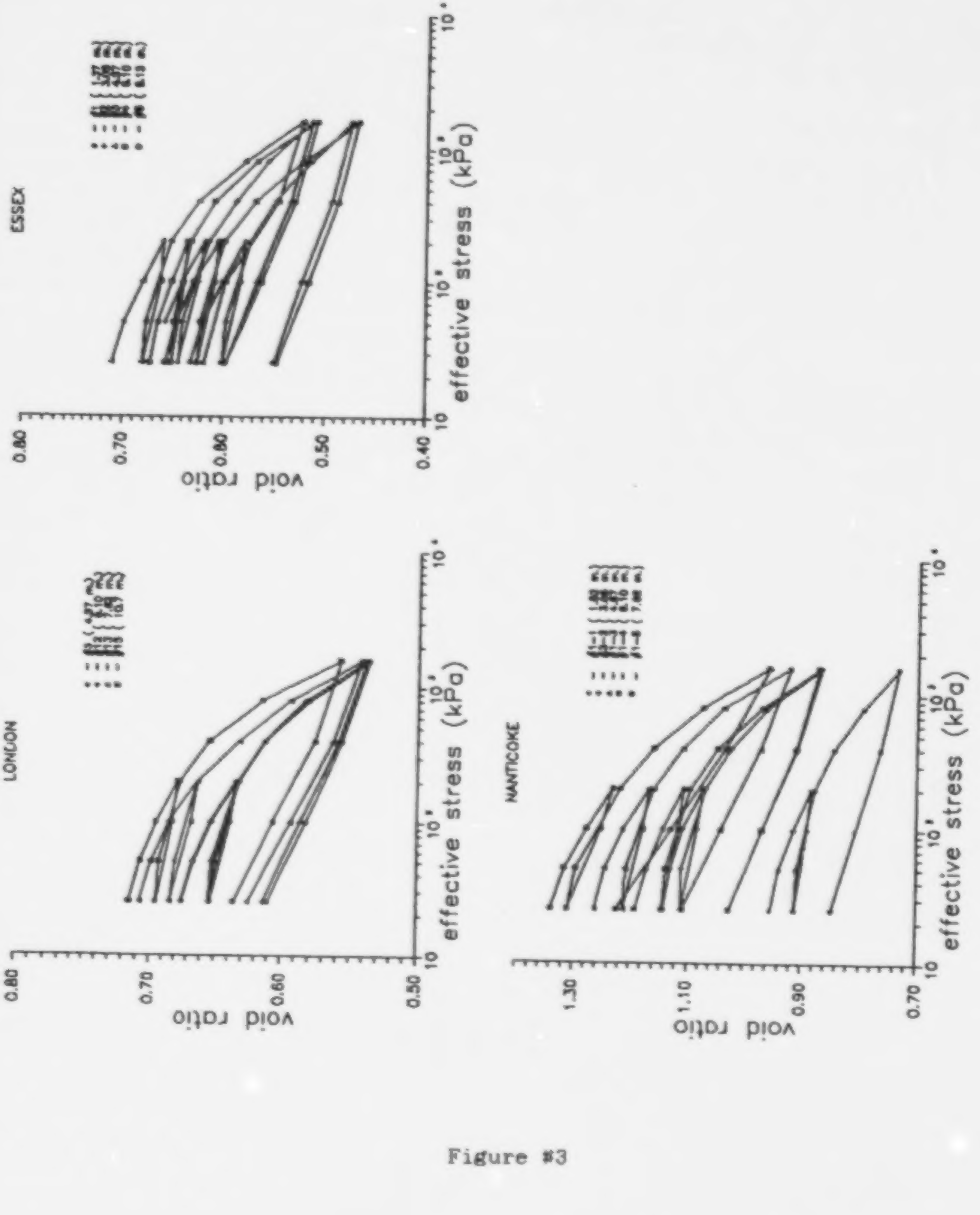

ESSEX
void ratio
0.80
0.70
0.60
0.50
0.40
effective stress (kPa)
10
10²
10³
10⁴
LONDON
void ratio
0.80
0.70
0.60
0.50
effective stress (kPa)
10
10²
10³
10⁴
NANTICOKE
void ratio
1.30
1.10
0.90
0.70
effective stress (kPa)
10
10²
10³
10⁴

Figure #3

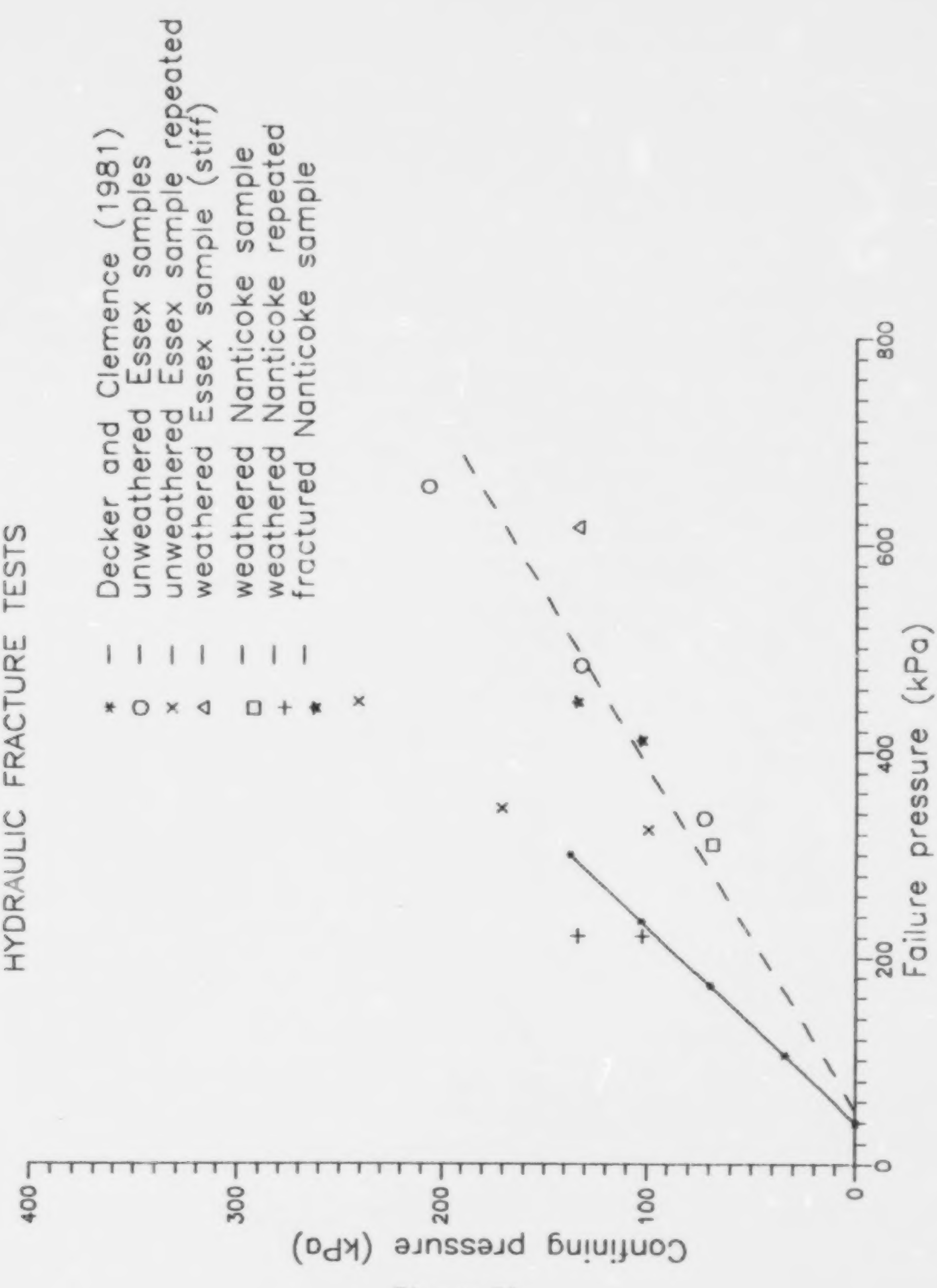
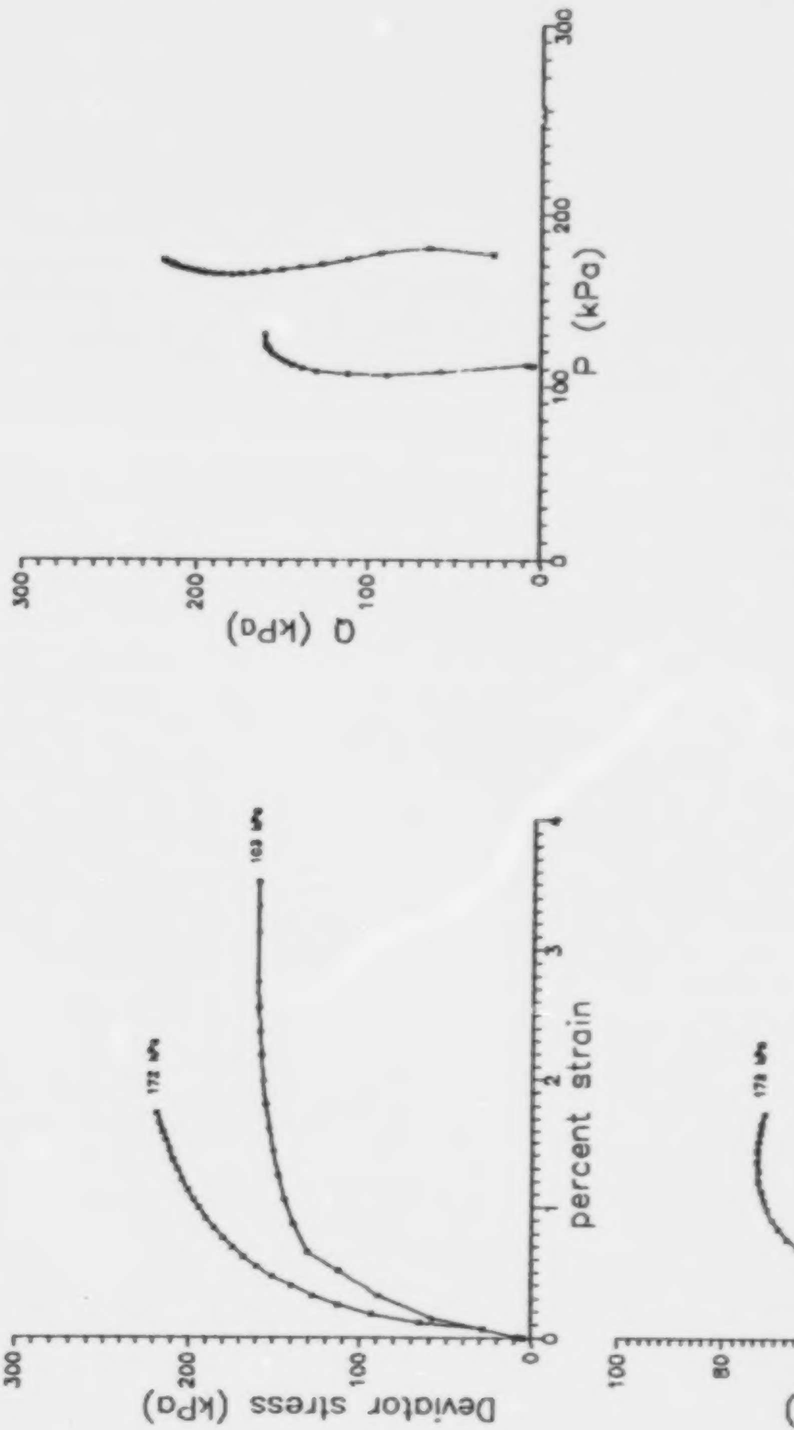
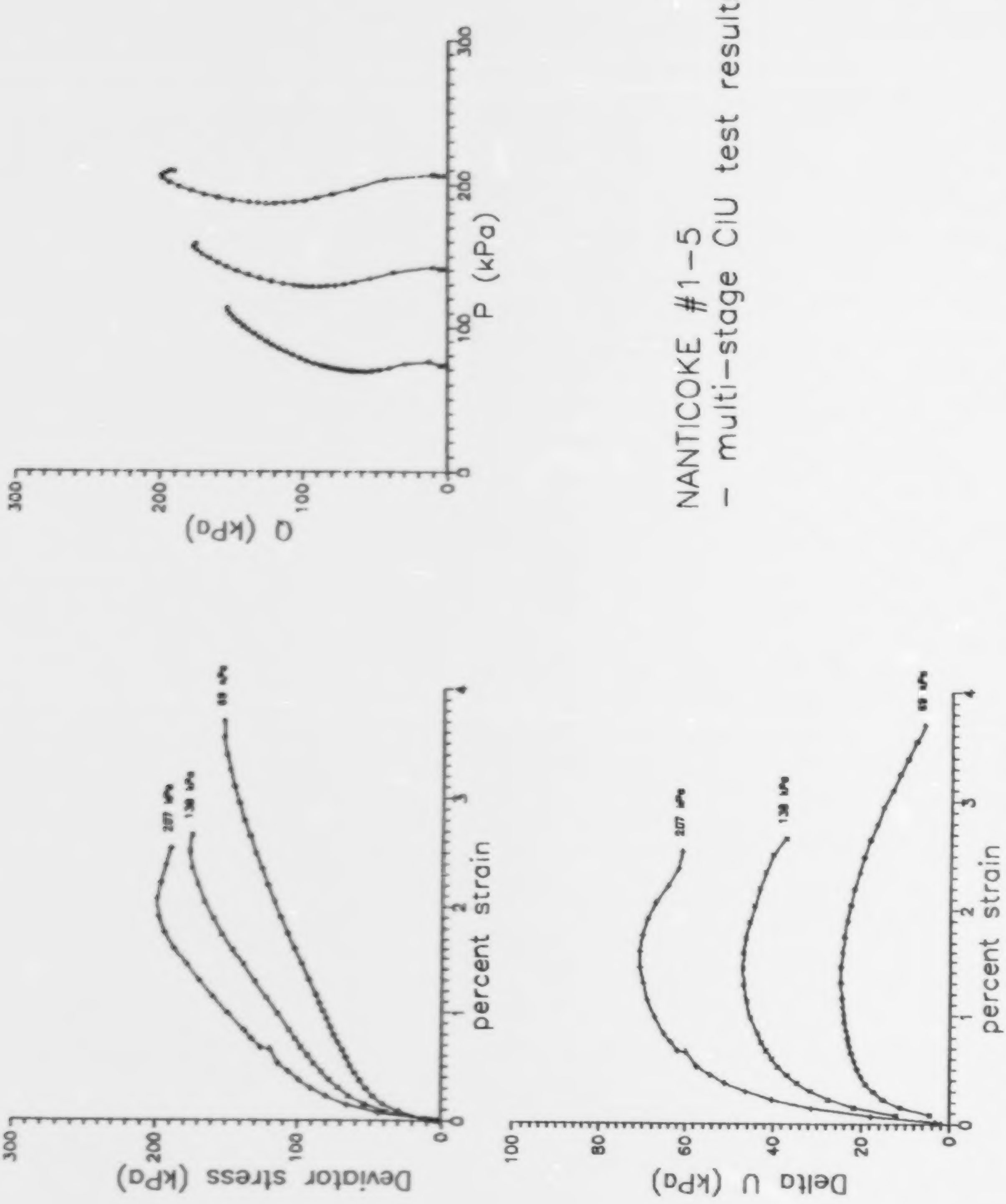

HYDRAULIC FRACTURE TESTS
* — Decker and Clemence (1981)
○ — unweathered Essex samples
× — unweathered Essex sample repeated
△ — weathered Essex sample (stiff)
□ — weathered Nanticoke sample
+ — weathered Nanticoke repeated
✱ — fractured Nanticoke sample
Confining pressure (kPa)
0
100
200
300
400
Failure pressure (kPa)
0
200
400
600
800

Figure #4



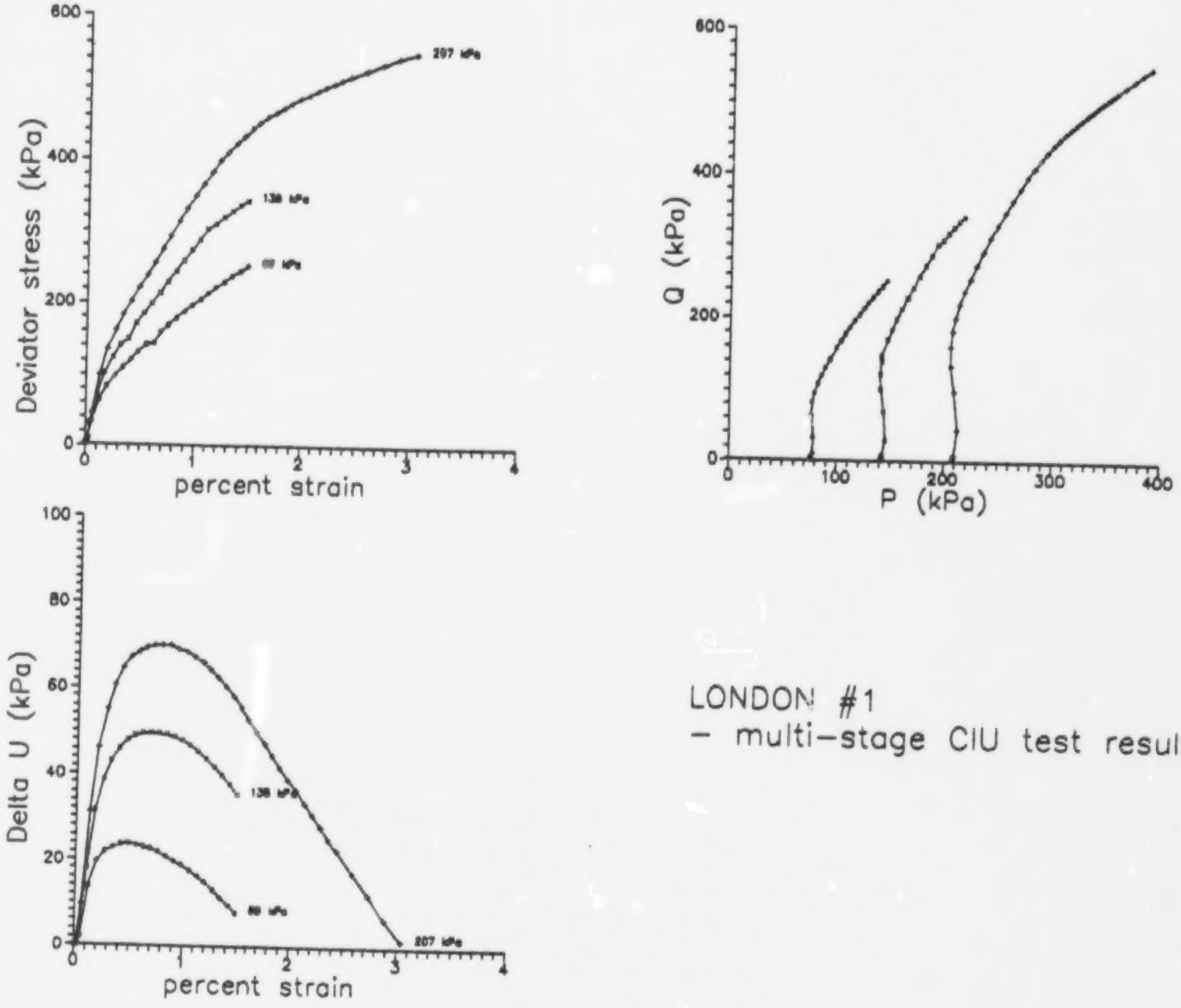
NANTICOKE #1-1 (103 kPa)
NANTICOKE #2-1 (172 kPa)
- multi-stage CIU test results

Figure #5



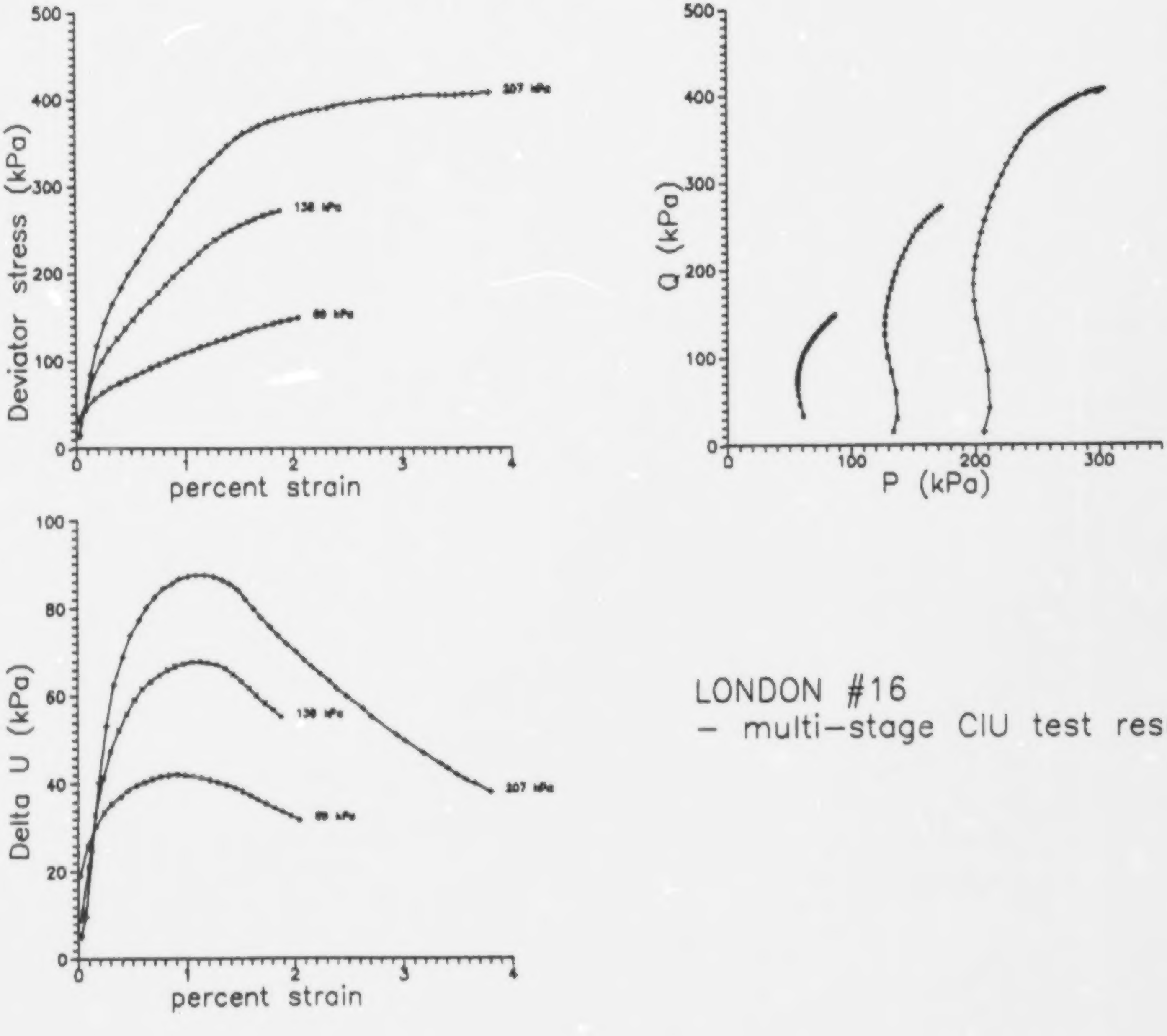
NANTICOKE #1-5
– multi-stage CIU test results

Figure #6



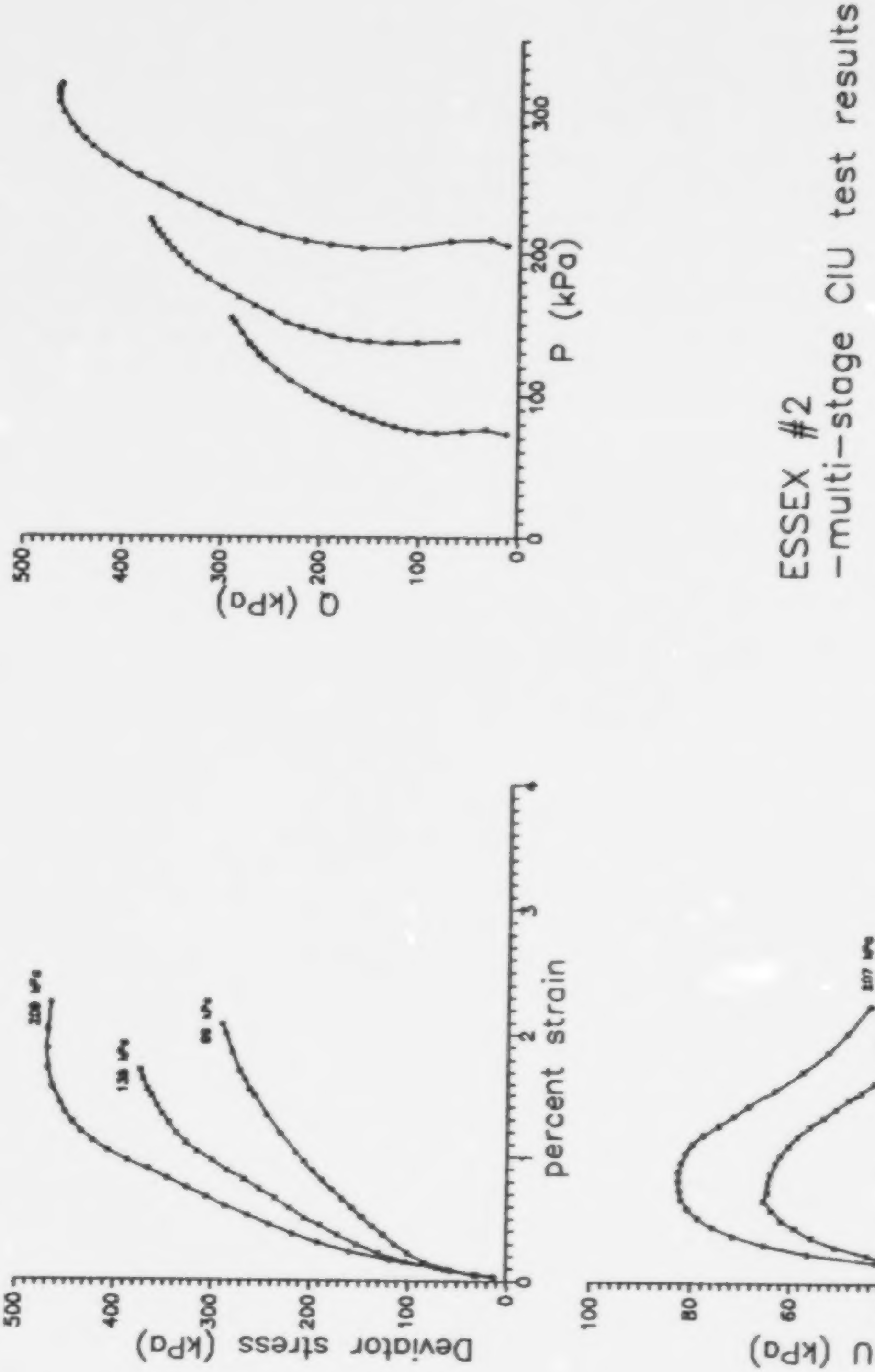
LONDON #1
– multi-stage CIU test results

Figure #7



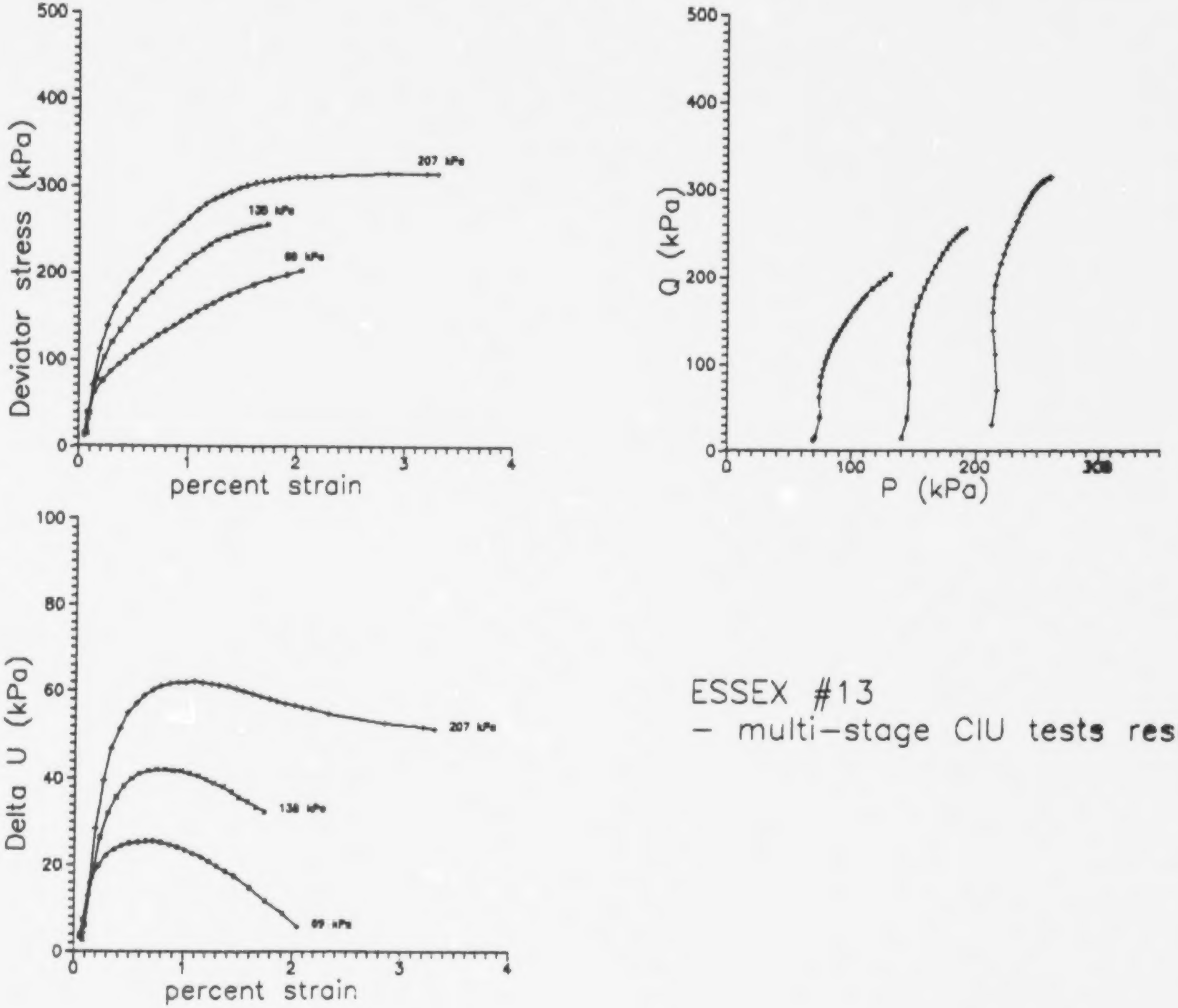
LONDON #16
- multi-stage CIU test results

Figure #8



ESSEX #2
-multi-stage CIU test results

Figure #8



ESSEX #13
– multi-stage CIU tests **results**

Figure #10

ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS

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Key words: Groundwater, Chloride Enrichment, Hydrochemistry

ABSTRACT

Shallow aquifer systems in southern Ontario frequently exhibit elevated chloride concentrations that locally exceed water quality guidelines. While in some cases the elevated chloride concentrations can be attributed to indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots.

At the University of Toronto, hydrochemical studies are in progress that aim to develop multi-parameter methods of identifying sources of groundwater contamination. Chemical parameters have included major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3, minor ions (Br, I, and F), and over 20 trace metals. Tritium has been used locally. To date the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary external sources of the chloride enrichment. A total of 110 domestic well water samples, 40 contaminant samples and 70 interstitial water samples have been collected and analyzed.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. In addition attempts have been made to characterize chemically the major sources of contamination in the area and, more importantly, to develop an understanding as to how the chemical characteristics of the contaminants are modified during transport through the shallow sub-surface. In previous work, the minor inorganic anions (I and F) have proved to the most reliable indicators of chloride origin, being particularly effective at distinguishing between bedrock and road de-icing chemicals as sources of saline water. In this work, which focuses on trace metal chemistry, few of the determinands have shown anomalously high concentrations in the chloride enriched groundwaters. Nevertheless, there is good evidence that Al, Ni , Ba, Cu, Zn and Pb may prove beneficial indicators of contaminant origin in specific situations.

INTRODUCTION

Despite the recent evidence of Kurtz and Morris (1983) the chloride ion is not generally regarded as a harmful constituent of water. Nevertheless its high solubility, chemically conservative behaviour and virtually ubiquitous association with hazardous chemicals give it the distinction of being a powerful and frequently used indicator of groundwater contamination. In southern Ontario, groundwaters from shallow aquifer systems regularly exhibit chloride ion concentrations in excess of 10 to 15 mg/L which is the anticipated background concentration in naturally evolving groundwaters (Howard, 1985). In many cases chloride levels exceed the maximum desirable concentration of 250 mg/L (MOE, 1984). While in some cases the elevated chloride concentrations can possibly be attributed to very local indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots (Howard et al., 1985).

In recent years the Groundwater Research Group at the University of Toronto has been engaged in a series of studies aimed at understanding the distribution, origins and behaviour of local shallow groundwaters containing elevated concentrations of chloride. The work is phased over three years and considerable data collection and analysis remain to be done. However, the ultimate, long-term objectives of the project are essentially

a) to determine natural background levels of specific major, minor and trace chemical constituents in local shallow groundwaters and to develop convenient multi-parameter methods of identifying sources of groundwater contamination;

b) to confirm that non-point source contaminants such as road de-icing chemicals and products of urban development are accumulating in the sub-surface environment, to determine their chemical behaviour and rates of chemical migration and to evaluate the magnitude and regional extent of the problem.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. In addition attempts have been made to characterize chemically the major sources of contamination in the area and, more importantly, to develop an understanding as to how the chemical characteristics of the contaminants are modified during transport through the shallow sub-surface. Parts of the study previously published have demonstrated the value of major anions as indicators of specific contaminant sources. This current paper concerns more recent work which has focused primarily on trace metal geochemistry. It describes the technical approach adopted for the study and summarizes some of the progress achieved. A location map showing the primary areas of investigation is shown on Figure 1.

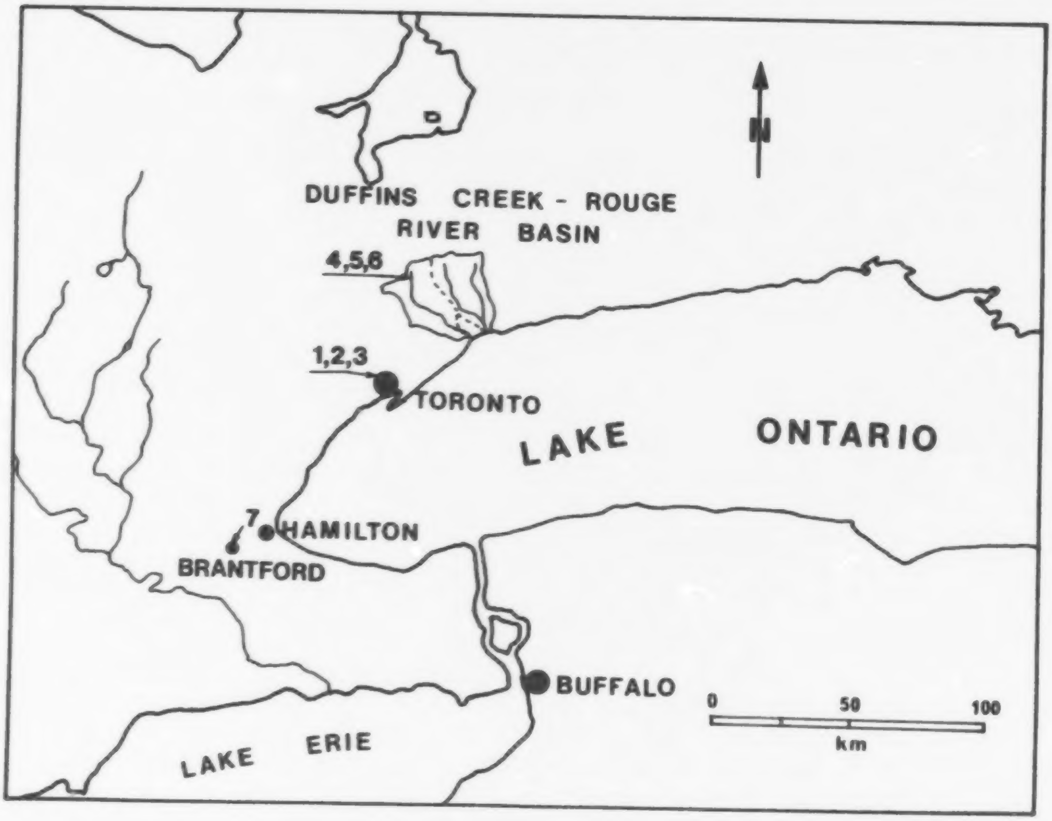

N
DUFFINS CREEK - ROUGE RIVER BASIN
4,5,6
1,2,3
TORONTO
LAKE ONTARIO
7
HAMILTON
BRANTFORD
BUFFALO
0
50
100
km
LAKE ERIE

Figure 1. Location map for seven auger sites

APPROACH AND ANALYTICAL PROCEDURES

To date the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary non-point sources of the chloride enrichment (Pilon and Howard, 1986 in press). A total of 110 domestic well water samples, 40 contaminant samples and 70 interstitial water samples have been collected and analyzed for a wide range of inorganic parameters. These include the major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3, minor ions (Br, I, and F), and over 20 trace metals. Tritium has been used locally.

Analytical procedures for pH, anions and major cations are summarized in Table 1. Several of the parameters together with all the trace metals were determined using the ARL 34000 inductively coupled plasma atomic emission spectrometer (ICP-AES) which is capable of providing rapid and simultaneous analysis of up to 31 elements. For this study, a total of twenty-two elements were selected for analysis; these are listed in Table 2 along with the instrument determination limit (5x theoretical detection limit).

Table 1. Analytical Methods for pH, Anion and Major Ion Analysis

Chemical Parameter	Analytical Method
pH	Specific ion electrode potentiometry
NO_3, F	Specific ion electrode potentiometry
Cl	Specific ion electrode potentiometry/ Potentiometric titration
I, Br	Colorimetry
SO_4	Colorimetry/ICP
HCO_3	Titration
Ca, Mg	ICP/Atomic absorption spectrophotometry
K, Na	Flame emission spectrophotometry

Each suite of samples submitted to the ICP laboratory was accompanied by a blank sample consisting of double deionized water which was filtered and prepared in a manner identical to the groundwater samples. The blank was used as an indicator of the amount of contamination introduced to the sample during laboratory preparation. A total of six blanks were submitted for trace element analysis and the results are shown in Table 3. For each element the average value of the blanks was determined and compared to the determination limit. For the twenty-two elements measured by ICP-AES, only five elements Fe, Mg, Ca, Cu, and Ba, exceeded the determination limit. As a result, corrections were made to these analyses. In addition to the blanks, NBS standards were also submitted for ICP checks.

To improve levels of determination using the ICP-AES, sample volumes in excess of 100mL were pre-concentrated prior to analysis. Approximately 100 mL of acidified, filtered water was boiled almost to dryness in a pyrex beaker. 0.5 mL of Ultrapure nitric acid and 1 mL of double distilled water were added to the beaker and the sample was once again evaporated to near dryness. In the final step, 0.5 mL of ultrapure nitric acid and 1 mL of double distilled water were added to the beaker and the sample was evaporated for approximately 5 minutes. Sample volume was then made to 10 mL in a 10 mL erlenmeyer flask.

Table 2. Parameters determined by ICP-AES analysis

Element Units	T.D.L. (mg/L)	D.L. (mg/L)	Element Units	T.D.L. (mg/L)	D.L. (mg/L)
Be	0.00029	0.001	Ca	0.0014	0.007
Ba	0.00025	0.001	Zn	0.004	0.02
Fe	0.0012	0.006	Cu	0.0023	0.0115
Cr	0.0024	0.012	Sb	0.0377	0.1885
S	0.0132	0.066	Pb	0.0460	0.23
Mg	0.0137	0.0685	Cd	0.0032	0.016
As	0.0226	0.113	Co	0.0034	0.017
V	0.0016	0.008	Ni	0.0137	0.0685
Se	0.0823	0.2115	P	0.0357	0.1785
Mo	0.0068	0.034	B	0.0045	0.0225
Al	0.0164	0.082	Mn	0.0006	0.0030

T.D.L.= Theoretical Detection Limit D.L = Determination Limit

Table 3. Results of Trace Element Analysis for Blanks

Element	Ave. of Six Blanks	5X T.D.L.	Element	Ave. of Six Blanks	5X T.D.L.
Be	0.0003	0.001	Ca	0.2691	0.0070
Ba	0.0020	0.001	Zn	0.0152	0.0200
Fe	0.0531	0.0060	Cu	0.0191	0.0115
Cr	0.0045	0.0120	Sb	0.0384	0.1885
S	0.0205	0.0660	Pb	0.0257	0.2300
Mg	0.0846	0.0685	Cd	0.0008	0.0160
As	0.0177	0.1130	Co	0.0027	0.0170
V	0.0056	0.0080	Ni	0.0139	0.0685
Se	0.0374	0.2115	P	0.0758	0.1785
Mo	0.0011	0.0340	B	0.0045	0.0225
Al	0.0594	0.0820	Mn	0.0001	0.0030

SAMPLING - PURPOSE AND PROCEDURES

Uncontaminated Well Waters

A primary focus of recent work has been to determine background levels of anion, major cation and trace constituents in naturally evolving uncontaminated groundwaters. These data are essential if contamination is to be clearly recognised and chemically characterised. This part of the study is being conducted in the Rouge River-Duffins Creek drainage basins (Sibul et al., 1977) where Beck (1985), Thompson et al. (1985), and Howard and Beck (1986) have provided a comprehensive major ion classification of shallow groundwaters. On the basis of this earlier work background concentrations of several major ion parameters were already apparent (Howard, 1985), and potential sampling sites were well documented.

Samples were collected from 110 of the 269 sites sampled by Beck (1985). Since both major ion and trace constituents were to be measured, two well water samples were obtained from each sample location. These were collected in 250 mL polyethylene bottles which had been prepared by rinsing in a 10 per cent nitric acid bath and thoroughly flushed with distilled water. One 250 mL sample was immediately filtered and acidified in the field for trace constituent analysis. Filtering was carried out under pressure using a 0.45 um cellulose acetate filter membrane and a hand pump. To avoid potential contamination by the membrane this was washed with 0.1 per cent ultrapure nitric acid and rinsed 3 times in double distilled water prior to use.

Potential Contaminant Sources

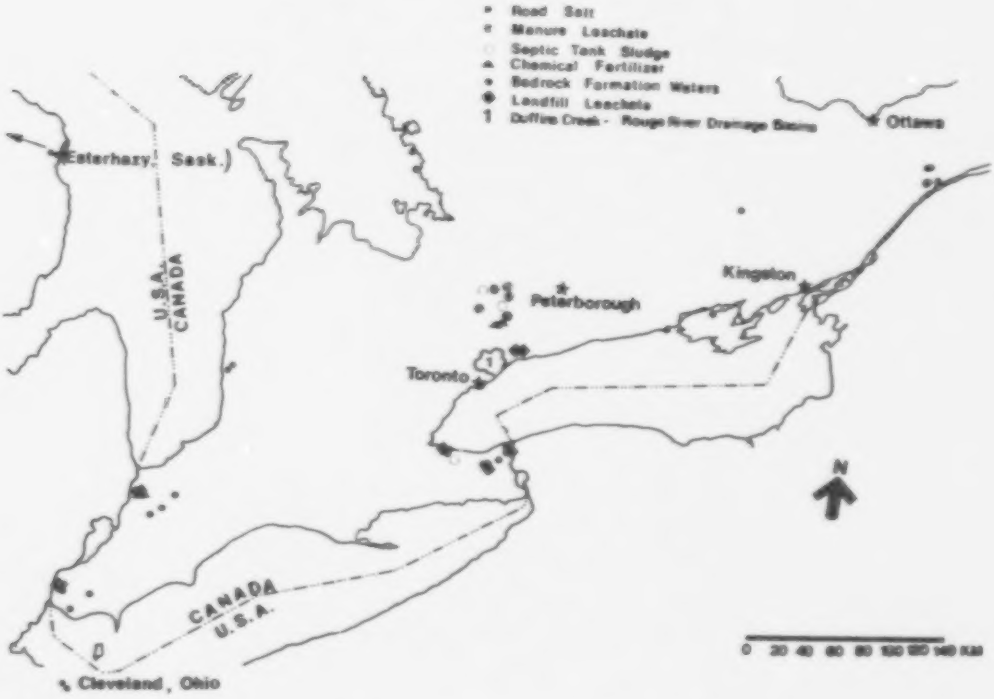
In an attempt to determine the geochemical characteristics of various contaminant sources in the region a wide range of samples were collected. A site map showing sample locations is shown on Figure 2. Part of this work was undertaken in cooperation with Hunter and Associates (Hunter and Associates, 1985) and has been published by Beck and Howard (1986). The types of sample included:

i) 8 samples of road salt (NaCl) from 4 different suppliers (Table 4);
ii) 4 samples of inorganic fertilizer from C.I.L. in Courtright, Ontario (including mono- and di- ammonium phosphate, prilled urea, and ammonium nitrate);
iii) 9 samples of human and livestock sludge obtained from liquid holding tanks, manure pits and manure spreaders;
iv) 5 landfill leachates obtained from collection systems at the Mountain Road, Glenridge Quarry and Brock West Landfill sites;
v) 14 samples of groundwater from southern Ontario bedrock locations.

Prior to chemical analysis, liquid sludge and leachate samples were processed using centrifuge and pressure filtration techniques to separate the liquid fraction. For ICP-AES analysis the samples were then acidified using Ultrapure nitric acid. Solid samples such as fertilizers and road salts were simply dissolved and acidified. In some cases the resulting solutions required considerable dilution due to extremely high sodium concentrations. Samples highly enriched in sodium (> 20,000 mg/L) tend to inhibit the nebulizer function in the ICP-AES to the extent that measurement of other elements becomes unreliable.

Table 4. Road De-icing Chemicals

Sample No.	Location	Source	Formation	Age
18, 22	Windsor,Ont.	Ojibway Mine	Salina	Silurian
19, 23	Goderich,Ont.	Goderich Mine	Salina	Silurian
21, 25	Esterhazy,Sask.	Potash Mine	Prairie	M. Devonian
20, 24	Cleveland,Ohio.	Cleveland Mine	Salina	Silurian



• Road Salt
▪ Manure Leachate
○ Septic Tank Sludge
▲ Chemical Fertilizer
• Bedrock Formation Waters
⬢ Landfill Leachate
1 Duffins Creek - Rouge River Drainage Basins
Ottawa
Esterhazy, Sask.)
U.S.A.
CANADA
Kingston
Peterborough
Toronto
1
N
CANADA
U.S.A.
Cleveland, Ohio
0 20 40 60 80 100 120 140 KM

Figure 2. Contaminant source location map

Interstitial Water Samples

While it may be possible to geochemically characterise the contaminants at source, most contaminants will undergo various geochemical transformations during sub-surface transport and ground water mixing. For example, while the gross impact of urban development on groundwater quality was recognised during the early stages of the project following a comprehensive survey of spring waters emanating along the Scarborough Bluffs (Howard et al., 1985; Pilon et al., 1985), specific sources of the contamination were not immediately apparent from the data. Thus in order to investigate more rigorously the degree and hydrogeochemical nature of contamination by urban development and similar non-point contaminant sources, an interstitial water sampling program was implemented involving a total of 20 holes at 8 sites. These sites are listed in Table 5 and are shown on the study area map in Figure 1.

Table 5. Auger Sites

Site	Location	Number of Auger Holes	Contaminant
1	Don Valley adjacent to the Parkway	8	Urbanization/ Road Salt
2	Don Valley-Seton Park	2	Urbanization/ Road Salt
3	Don Valley-Snow Dump	5	Urbanization/ Road Salt
4	Milliken	3	Fallow field/ Control Site
5	Ballantrae-Hwy 48	2	Road Salt
6	Markham	1	Cropland Nitrogen Fertilizer
8	Brantford	3	Cropland Nitrogen Fertilizer

The interstitial waters were extracted from sediment samples collected from the unsaturated zone above the water table. A gasoline powered auger, Dig-R-Mobile, was used to drill to the desired sample depth. The auger rods were then removed and a hand operated auger was used to obtain a partially saturated sediment sample. This sample was placed in a polyethylene bag, sealed, labelled, and packed in ice for transport to the laboratory. Interstitial water was extracted from the sediment samples with minimum delay (usually beginning the same day as collection) so as to avoid changes in the composition of the water (Barber et al., 1977). This was achieved by centrifuging the samples in specially designed Nalgene cups for 30 to 60 minutes at a speed of 2500 to 3500 rpm and a temperature of 4°C. The volume of interstitial extracted depends on the period of centrifugation, weight of sample, pore size distribution of the material, the degree of initial saturation, and the centrifuge dimensions (Edmunds and Bath, 1976). In general, interstitial water recoveries varied between 10 and 350 mL per depth sampling increment. Occasionally samples produced less than 1 mL and could not be used for analytical purposes.

To obtain information regarding the geochemical composition of sediments sampled, a total of thirty-five soil samples were collected for neutron activation analysis. Both short and long lived isotopes were measured and these are listed in Table 6.

Table 6. Elements determined during Neutron Activation Analysis of the Sediments

Short-lived Isotopes	Long-lived Isotopes
Ba	Fe
Ti	Sb
Mg	Br
Na	Cr
Cl	Zn
Al	
Ca	
Mn	
V	

RESULTS AND DISCUSSION

Introduction

With one field season remaining, several elements of the investigation await completion. Furthermore, whilst a considerable volume of chemical data has been collected, many samples remain to be analyzed and the currently available results are in various stages of processing, plotting and interpretation. Thus while substantial progress has been achieved during the study, it must be emphasised that the results presented and discussed below are preliminary and may be subject to refinement and possible revision as further data become available.

Background Chemistry of Uncontaminated Groundwaters

The background chemistry of uncontaminated waters will vary according to the chemistry of the input water (aquifer recharge), the geochemistry of the aquifer matrix and the degree of hydrochemical evolution the water undergoes as it moves through the system. Early studies aimed at understanding the hydrochemical evolution of groundwaters in surficial sediments were initiated by Beck (1985) and have been extended as part of the present investigations.

Major and Minor Ions

The work of Beck (1985) focused on major and minor ion parameters. This and subsequent work (Howard, 1985; Howard and Beck, 1986) showed that ground waters migrating regionally in shallow unconsolidated sediments of southern Ontario evolved from a Type 1A through 2A and 3A to a Type 4A water with cation exchange as the primary modifying influence. During this chemical evolution, dissolution of indigenous soluble salts, a commonly recognised process in large sedimentary basins, was found to have only minor importance. Table 7 shows typical background concentrations of major and minor ion constituents in uncontaminated Type 1A through Type 4A groundwaters of the Duffins Creek / Rouge River drainage basins. The data suggest that chloride concentrations as low as 15-20 mg/L (above the maximum levels observed) may be regarded as a positive indication of contamination.

Table 7. Typical Major and Minor Ion Background Hydrochemistry of Naturally Evolving Groundwaters

		EVOLVING WATER TYPE			
		1A	2A	3A	4A
Parameter	Unit				
Ca	mg/L	90	40	30	20
Mg	mg/L	20	20	15	10
Na	mg/L	5	20	30	50
K	mg/L	2	2	2	2
HCO_3	mg/L	350	250	250	250
Cl	mg/L	<5	<10	<15	<15
SO_4	mg/L	20	5	5	5
NO_3	mg/L	<10	<10	<10	<10
F	mg/L	<0.2	0.2	0.25	>0.25
I	mg/L	<0.005	<0.01	<0.02	>0.015

Trace Metals

With respect to trace constituents, Tables 8a, 8b and 8c present a statistical summary of the trace metal data for the presumed uncontaminated 1A, 2A and 3A groundwaters. Since the occasional anomalous trace constituent analysis can result in a distorted mean concentration and relatively high standard deviation, the general practice has been to use median values and ranges to compare water types. There are currently insufficient data to characterise confidently the trace metal content of Type 4A waters.

Type 1A waters which represent the younger, recharge waters tend to display lower concentrations of most trace constituents relative to the older waters 2A and 3A. Minor exceptions include Al, Fe, and Ba which occasionally show elevated concentrations. With the exception of Fe and Mn, all trace constituents present above determination limits, occur below either the maximum acceptable (MAC) or the maximum desirable (MDC) concentrations as recommended by the Ontario Ministry of the Environment (MOE, 1984). All Type 1A waters exceeded the MDC limit of 0.3 mg/L for Fe and one sample exceeded the MDC limit of 0.05 mg/L for Mn.

Type 2A waters which are older than Type 1A, but pre-date Types 3A and 4A, contain concentrations of trace elements which generally fall between those of 1A and 3A. Type 2A waters show slightly higher (median) concentrations of Mn, P, Cu, and B relative to Type 1A waters. Concentrations of Al, Fe, and Ba in these waters are lower than in Type 1A waters.

Type 3A waters contain elevated concentrations of Mn, P, Mo, Cu, and B relative to Type 1A and 2A waters. These waters also show concentrations of Fe and Al similar to those of Type 1A waters. Mn concentrations were highest in Type 3A groundwaters (ranging from 0.0319 to 0.2363 mg/L) with 4 of 6 samples exceeding the MDC of 0.05 mg/L for Mn. In addition, 3 of the 6 Type 3A samples exceeded the MDC of 0.3 mg/L for Fe.

In summary, two general trends can be identified in the uncontaminated groundwaters during transition from Type 1A to 3A waters. These are as follows:

a) increasing P, Mn, Mo, Cu, and B concentrations; and,

b) decreasing Ba concentrations.

In all three water types concentrations of Ni, Pb, As, Se, Sb were found to occur at concentrations less than the determination limit.

Table 8a Statistical Data for Type 1A Groundwaters

Element	N	$\bar{x}$	σ	range	median
Mn	3	0.0480	0.0419	0.0131-0.1070	0.0241
P	3	<0.0178	--	<0.0178-0.0323	<0.0178
Mo	3	<0.0034	--	<0.0034	<0.0034
Al	3	<0.0082	--	<0.0082-0.1461	<0.0082
Zn	3	0.1797	0.2338	0.0094-0.5103	0.0193
Ni	3	<0.0068	--	<0.0068	<0.0068
Fe	3	0.4863	0.1802	0.3580-0.7412	0.3597
Pb	3	<0.023	--	<0.023	<0.023
Cu	3	0.0238	0.0122	0.0083-0.0382	0.0249
Co	3	<0.0017	--	<0.0017	<0.0017
Cr	2	0.0023	0.0021	0.0002-0.0043	0.0029
Cd	3	<0.0016	--	<0.0016	<0.0016
As	3	<0.0113	--	<0.0113	<0.0113
Se	3	<0.0211	--	<0.0211	<0.0211
Sb	3	<0.0188	--	<0.0188	<0.0188
V	3	0.0015	0.0007	0.0008-0.0025	0.0011
B	3	<0.0001	--	<0.0001	<0.0001
Ba	3	0.0941	0.0487	0.0258-0.1361	0.1203
Be	3	<0.0001	--	<0.0001-0.0008	<0.0001

-- Not Calculated Units mg/L

Table 8b Statistical Data for Type 2A Groundwaters

Element	N	$\bar{x}$	σ	range	median
Mn	3	0.0310	0.0035	0.0276-0.0357	0.0296
P	3	0.0512	0.0328	0.0273-0.0976	0.0288
Mo	3	<0.0034	--	<0.0034	<0.0034
Al	3	0.0114	0.0062	0.0038-0.0191	0.0115
Zn	3	0.1578	0.1536	0.0074-0.3687	0.0974
Ni	3	<0.0068	--	<0.0068	<0.0068
Fe	3	0.3095	0.2444	0.0180-0.6160	0.2946
Pb	3	<0.023	--	<0.023	<0.023
Cu	3	0.0242	0.0180	0.0069-0.0490	0.0167
Co	3	<0.0017	--	<0.0017	<0.0017
Cr	3	<0.0012	--	<0.0012-0.0005	<0.0012
Cd	3	<0.0016	--	<0.0016	<0.0016
As	3	<0.0113	--	<0.0113	<0.0113
Se	3	<0.0211	--	<0.0211	<0.0211
Sb	3	<0.0188	--	<0.0188	<0.0188
V	3	0.0017	0.0010	0.0010-0.0031	0.0010
B	3	0.0283	0.0051	0.0213-0.0333	0.0303
Ba	3	0.1240	0.0253	0.1019-0.1595	0.1019
Be	3	<0.0001	--	<0.0001-0.0002	<0.0001

-- Not Calculated Units mg/L

Table 8c Statistical Data for Type 3A Groundwaters

Element	N	$\bar{x}$	σ	range	median
Mn	6	0.0949	0.0703	0.0319-0.2363	0.0581
P	6	0.1676	0.0970	0.0508-0.3591	0.1493
Mo	2	0.0090	0.0053	0.0037-0.0143	0.0090
Al	4	0.0504	0.0197	0.0191-0.0745	0.0538
Zn	6	0.0666	0.0690	0.0031-0.2010	0.0455
Ni	6	<0.0068	--	<0.0068	<0.0068
Fe	6	0.3833	0.2061	0.0603-0.6080	0.4154
Pb	6	<0.023	--	<0.023	<0.023
Cu	6	0.0471	0.0405	0.0105-0.1267	0.0351
Co	6	<0.0017	--	<0.0017	<0.0017
Cr	6	<0.0012	--	<0.0012-0.0129	<0.0012
Cd	6	<0.0016	--	<0.0016	<0.0016
As	6	<0.0113	--	<0.0113	<0.0113
Se	6	<0.0211	--	<0.0211	<0.0211
Sb	6	<0.0188	--	<0.0188	<0.0188
V	6	0.0011	0.0004	0.0008-0.0019	0.0009
B	6	0.0870	0.2080	0.0473-0.1137	0.0905
Ba	6	0.1970	0.2355	0.0685-0.7161	0.0836
Be	6	<0.0001	--	<0.0001	<0.0001

-- Not Calculated Units mg/L

Contaminant Sources

A total of 43 potential contaminants were submitted for major and minor ion analyses, while 17 were submitted for trace constituent analysis. Samples submitted for trace constituent analysis included 1 landfill leachate, 9 bedrock waters, 4 inorganic fertilizers and 3 road de-icing chemicals. Site locations are shown on Figure 2. The major, minor and trace chemistry of each contaminant is discussed below.

Road De-icing Chemicals

A 5 % solution of NaCl road de-icing chemical was found to contain 20,250 mg/L Na, 30,860 mg/L Cl together with minor amounts of SO_4 (222 mg/L) and Ca (62.5 mg/L). The 5 % solution of $CaCl_2$ road de-icing chemical contained 12,890 mg/L Ca, 25,892 Cl with minor associated amounts of Na (550 mg/L) and SO_4 (25.8 mg/L). Both the NaCl and the $CaCl_2$ displayed similar trace element impurities as shown in Table 9. The 5 % solution of sodium chloride is distinguished from the bedrock waters, leachate and inorganic fertilizers (see below) by elevated concentrations of Al, Ni, Fe, Cu, and Ba. Likewise, $CaCl_2$ (5 % solution) also contains similar elevated concentrations of Ni and Fe but is distinguished from NaCl by lower concentrations of Al and Ba and a considerably higher concentration of Cu. Concentrations of Mn, Pb, Co, Cr, Cd, Se, Sb, B, V, As, Zn, P and Be were below ICP-AES determination limits for both the NaCl and $CaCl_2$ chemicals.

Table 9 Trace Constituents in Chemical Road De-Icing Chemicals

Element	NaCl 5 % Solution (mg/L)	$CaCl_2$ 5 % Solution (mg/L)
Al	166.7-181.0	92.1
Ni	42.3- 58.9	57.9
Fe	42.2- 58.8	57.8
Cu	98.2-154.5	251.9
Ba	7.4- 15.9	4.8

Fertilizers

The four inorganic fertilizers analyzed (mono- and di- ammonium phosphates, prilled urea, and ammonium nitrate) were found to exhibit considerable variations in their major and minor ion chemistry most likely due to the fact that each fertilizer is made to replace specific macro- and micronutrients in the soil. For example, nitrate concentrations vary from 26 mg/L in the prilled urea to 35,000 mg/L in the ammonium nitrate, while mono- and di- ammonium phosphate fertilizers contain notably elevated concentrations of Na (112 - 143.75 mg/L) and SO_4 (1772.6 - 3220 mg/L). Chloride concentrations were generally found to be low (typically <10 mg/L) although di-ammonium phosphate did show a concentration of 36 mg/L.

The four inorganic fertilizers also exhibit varying concentrations of trace constituents. As would be expected, mono- and di- ammonium phosphate fertilizers are distinguished from all other analysed contaminants and fertilizers by the presence of elevated concentrations of P (10^3 mg/L). These fertilizers also show elevated concentrations Mo and Cr. By comparison, ammonium nitrate and prilled urea are characterised by elevated concentrations of Al, Se, and Sb.

Landfill Leachate

As expected, the five landfill leachates submitted for major and minor ion analysis contain elevated concentrations of Cl (between 480 and 685 mg/L) and NO_3 (between 26.5 and 145 mg/L). As such, these leachates are readily distinguished from road de-icing chemicals and inorganic fertilizers, neither of which would normally exhibit high concentrations of both anions. More surprising are the relatively low levels of trace metals found in the leachates (Table 10). Leachate sampled from the gatehouse well in the Mountain Road Landfill site (Table 10) was found to contain very low levels of P, Zn, Fe, and As relative to the other contaminants investigated. Trace constituents Mn, Mo, Al, Ni, Pb, Co, Cr, Cu, Cd, Be and V were all below determination limits. The trace constituents present in highest concentrations were B (1.45 mg/L) and Ba (.1098 mg/L) but these concentrations are comparable to those present in bedrock waters sampled from domestic wells.

Table 10 Trace Constituents in Landfill Leachate

Element	Typical Landfill Leachate Composition* (mg/L)	Mountain Rd. Landfill Leachate Composition (mg/L)
As	0.038	0.1140
Al	0.27	<0.0082
Ba	0.08	0.1078
Be	0.025	<0.0001
B	4.5	1.4552
Cd	0.0037	<0.0016
Cr	0.053	<0.0012
Cu	0.024	<0.0012
Fe	24	<0.0006
Pb	0.054	<0.023
Mn	0.6	<0.0003
Mo	0.013	<0.0034
Ni	0.069	<0.0068
V	**	<0.0008
Zn	0.5	0.0239

** Not Detected   * Daniel and Liljestrand (1984)

Bedrock Waters (Domestic Wells)

Low permeability bedrock formations commonly contain groundwaters with elevated major and minor ion concentrations. Southern Ontario is no exception. Occasionally groundwaters from bedrock formations leak into overlying surficial sediments where they cause contamination. To date, sampling of bedrock waters has been largely restricted to deep domestic wells where groundwater salinities tend to be unrepresentatively low. Nevertheless, some samples have shown Cl concentrations as high as 966.54 mg/L with Na up to 562.5 mg/L. SO_4 concentrations in the bedrock waters are generally low (31.6-34.3 mg/L) which may be a consequence of sulphate reduction. This conclusion appears to be supported by moderate to high concentrations of Mn (0.0469 - 4.8031 mg/L) and Fe. In general Zn, B and Ba are present in concentrations which are higher than landfill leachates but lower than other contaminants. The trace constituents P, Mo, Al, Ni, Pb, Co, Cr, Cd, As, Se, Sb, Be, Cu, and V are present in concentrations below determination limits for these elements.

Interstitial Waters

Urban road sites

The study of interstitial waters at urban road sites has revealed considerable contamination by road de-icing chemicals and other products of urban development. As shown in Figures 3 and 4 these waters may contain between 10^3 and 10^4 mg/L Cl and 10^3 mg/L Na as compared to concentrations of less than 10^2 mg/L Cl and less than 10^2 mg/L Na for interstitial waters from rural road sites. The elevated concentrations of Na and Cl are comparable to the concentrations of Na and Cl in seawater (10,500 mg/L and 19,000 mg/L respectively). One sample located approximately 100 m downslope from a ramp on the Don Valley Parkway

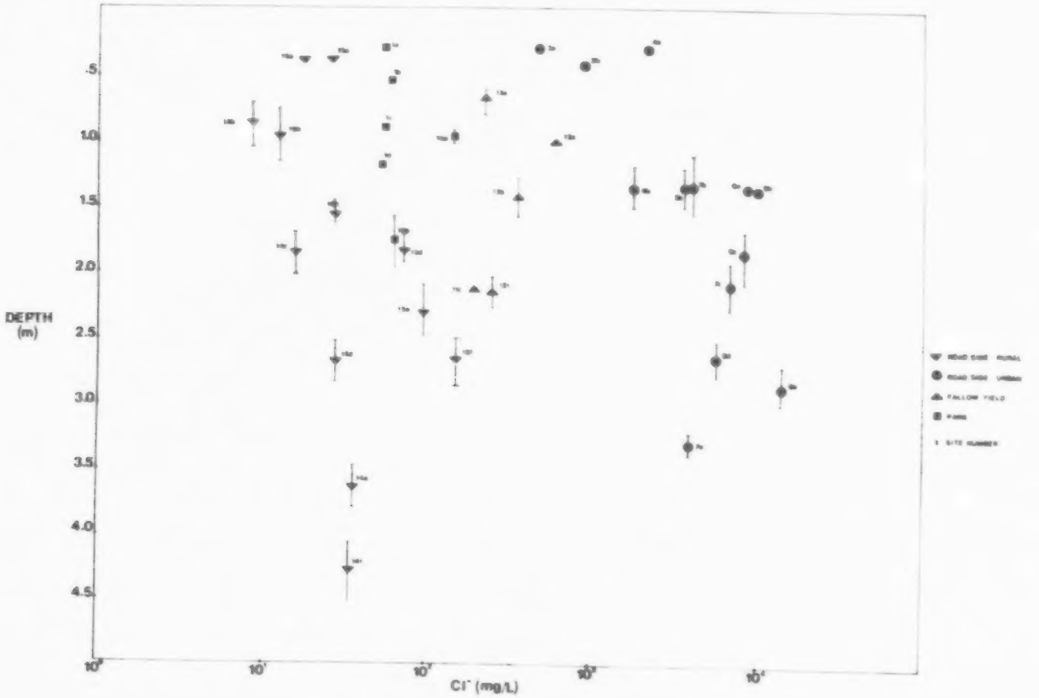


Figure 3. Plot of chloride concentration vs. depth

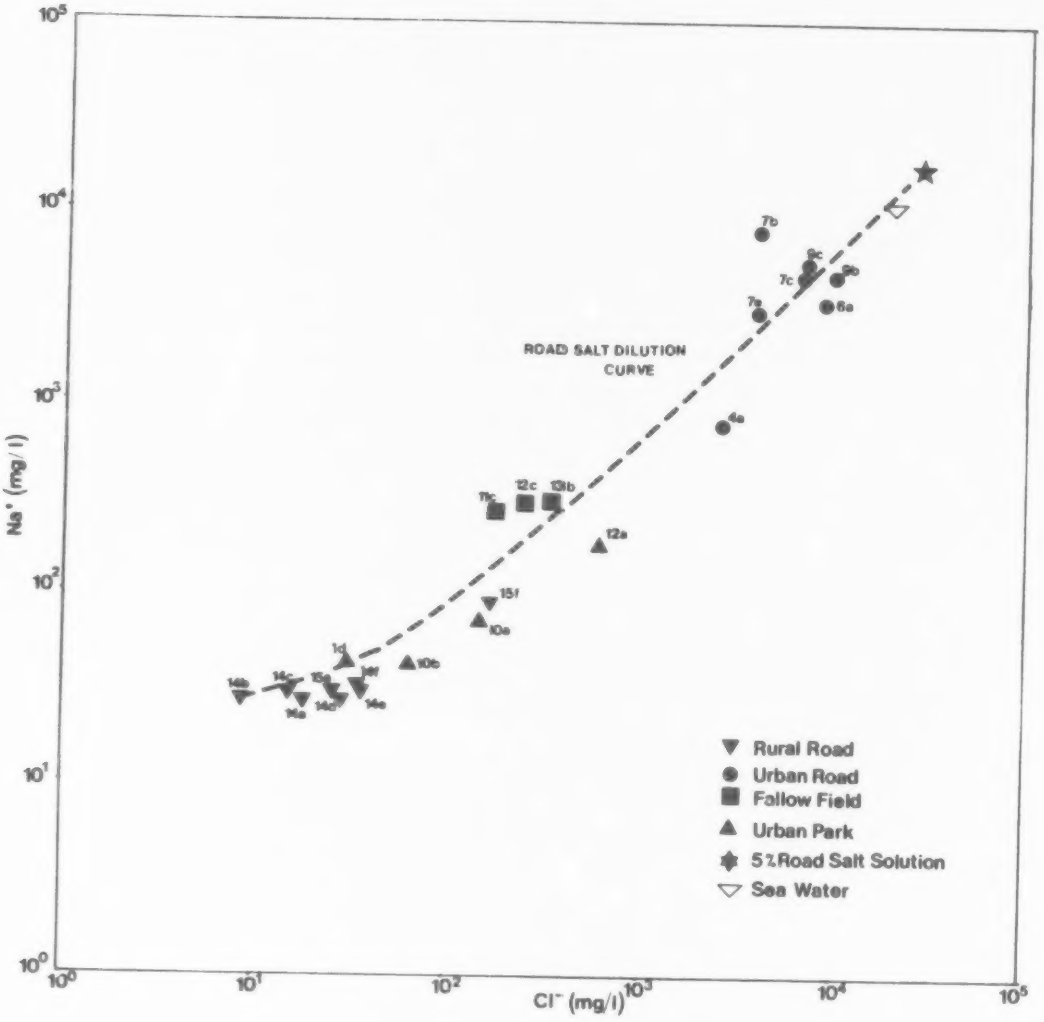


Figure 4. Plot of chloride vs sodium concentration

at a depth of 2.85m contained chloride in excess of 13,000 mg/L. Extremely elevated chloride levels were measured in interstitial waters sampled as deep as 3.3m below the surface.

Trace constituent analyses of interstitial water samples from urban road sites (Table 11) reveal elevated concentrations of Mn, P, Al, Fe, Pb, Cr, As, Se, Sb, Ba relative to all other study sites. Comparison to Table 9 suggests that while road de-icing chemicals may account for enrichment in Al, Fe and Ba other factors must be responsible for the elevated concentrations of the other elements.

Table 11 ICP-AES Results for Site Representative Samples (Units mg/L)

Site Sample	Cropland (25A)	Fallow Field (11B)	Rural Road (15C)	Snow Dump (8A)	Urban Road (7E)	Parkland (10A)
Mn	0.0312	0.0067	0.0121	0.6012	0.1566	0.0389
P	0.2412	0.1297	0.1853	2.4199	2.4199	0.1326
Mo	<0.0034	0.0004	0.0052	0.0319	0.0099	0.0081
Al	0.1334	0.0641	0.1137	17.8170	0.0819	0.0299
Zn	0.0983	0.0183	0.0492	0.4995	0.0370	0.0125
Cd	<0.0016	<0.0016	0.0007	0.0126	<0.0016	<0.0016
As	<0.0113	0.0301	0.0433	0.0915	0.0619	0.0513
Se	<0.0211	0.0432	0.0197	0.0871	0.0564	0.0742
Sb	<0.0188	0.0569	0.0510	0.0846	0.0748	0.0548
V	<0.0008	0.0032	0.0026	0.1443	0.0032	0.0007
Ni	<0.0068	0.0111	0.0211	0.0581	0.0143	0.0123
Fe	0.1440	0.0006	0.0176	61.9589	0.0387	0.0006
Pb	<0.023	0.0147	0.0086	1.8708	0.0161	0.0030
Cu	0.0214	0.0560	0.3540	0.6051	0.2245	0.0207
Co	<0.0017	0.0018	0.0005	0.0096	0.0014	<0.0017
Cr	<0.0012	0.0061	0.0024	0.0713	0.0052	0.0039
B	0.0366	0.0121	0.0166	0.2334	0.1525	0.1068
Ba	0.0391	0.0539	0.0099	0.2535	0.3364	0.0855
Be	<0.0001	0.0001	<0.0001	0.0130	0.0001	0.0001

Urban Snow Dump Site

A similar degree of contamination is seen in interstitial waters sampled from a site where snow removed from city streets and parking lots is dumped. These waters contain elevated concentrations of Cl (10^3 mg/L), Na (10^2 to 10^3 mg/L) and SO_4 (10^2 mg/L) relative to the urban park, and cropland sites. Trace element analyses indicate relatively high concentrations of Mn, P, Al, Zn, Fe, Pb, Cu, Cr, V, B and Be. It is suggested that the enrichment in trace constituents may be related to the source of the snow (Scott, 1979). Snow removed from streets would contain particulates enriched in heavy metals such as Fe, Pb, and Cu. When the snow melts, the particulates remain and accumulate in the soil column. Scott (1979) indicated that dumps receiving their snow from streets had a higher accumulation rate of Na, Cl, and Pb than did those snow dumps receiving their snow from parking lot dumps.

Rural Road Sites

Interstitial waters from the rural road sites contain Cl (10^1 to 10^2 mg/L), Na (10^1 mg/L) and SO_4 (10^1mg/L) concentrations which are considerably lower than those of the urban road site interstitial waters. Trace constituent analyses are comparably low with only P , Al, and Cu displaying significant concentrations. Al and Cu are present in high concentrations of road salts while P is a major constituent of inorganic fertilizers .

Cropland and Fallow Field Sites

Both cropland and fallow field interstitial waters contain similar concentrations of NO_3, K and Ca. However, the fallow field samples contain elevated concentrations of Cl (10^2 mg/L) and Na (10^2 mg/L) as compared with the cropland samples which have Cl and Na concentrations of 10^1 mg/L and 10^1 mg/L respectively. This may be more a reflection of local geological conditions than the nature of the contamination.

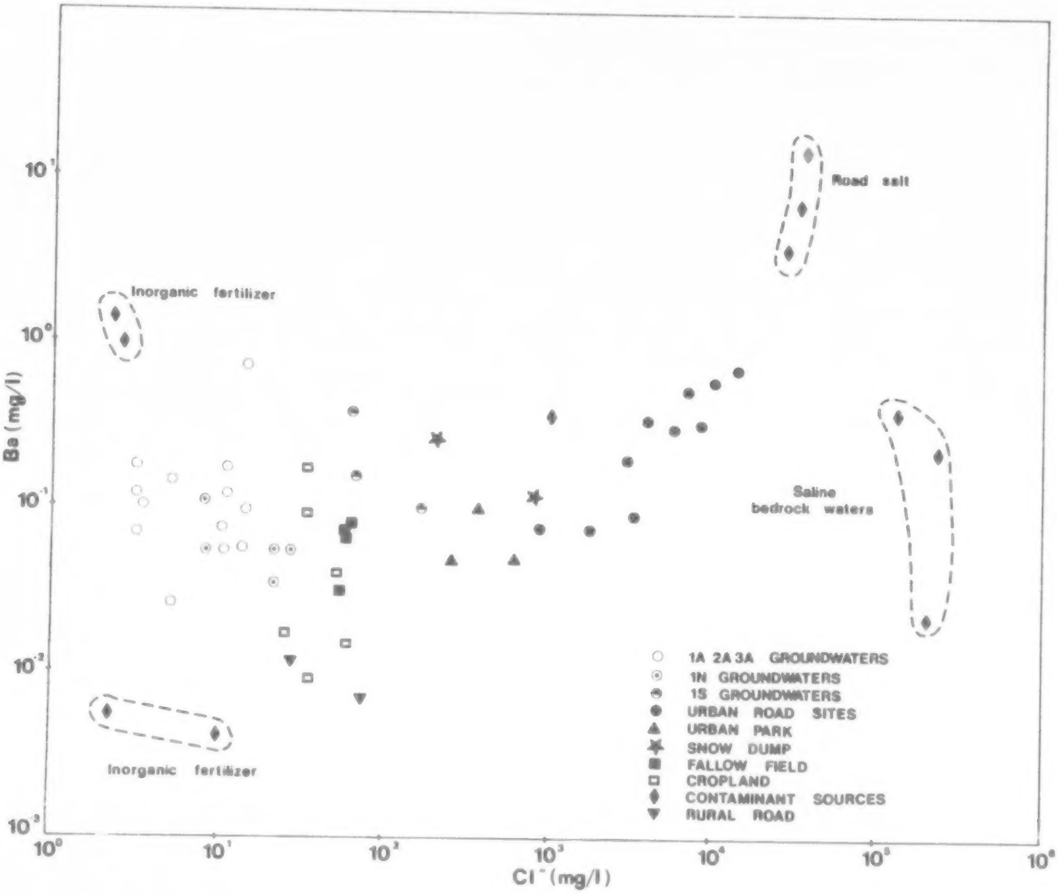


Figure 5. Plot of barium vs chloride concentration

Local geological conditions also play an important role in the geochemical modification of contaminants as they move through the shallow sub-surface. For example, interstitial waters sampled from cornfields contain moderate concentrations of Mn, P, Zn, Fe, Cu, B relative to the other sites investigated, but elements such as Mo and Cr evident in the fertilizers (see above) are not found to be present. This type of process is further illustrated by Figures 5 and 6 which show how concentrations of Ba and Cu in contaminant sources are, in many cases, notably different from concentrations present in the contaminated groundwaters.

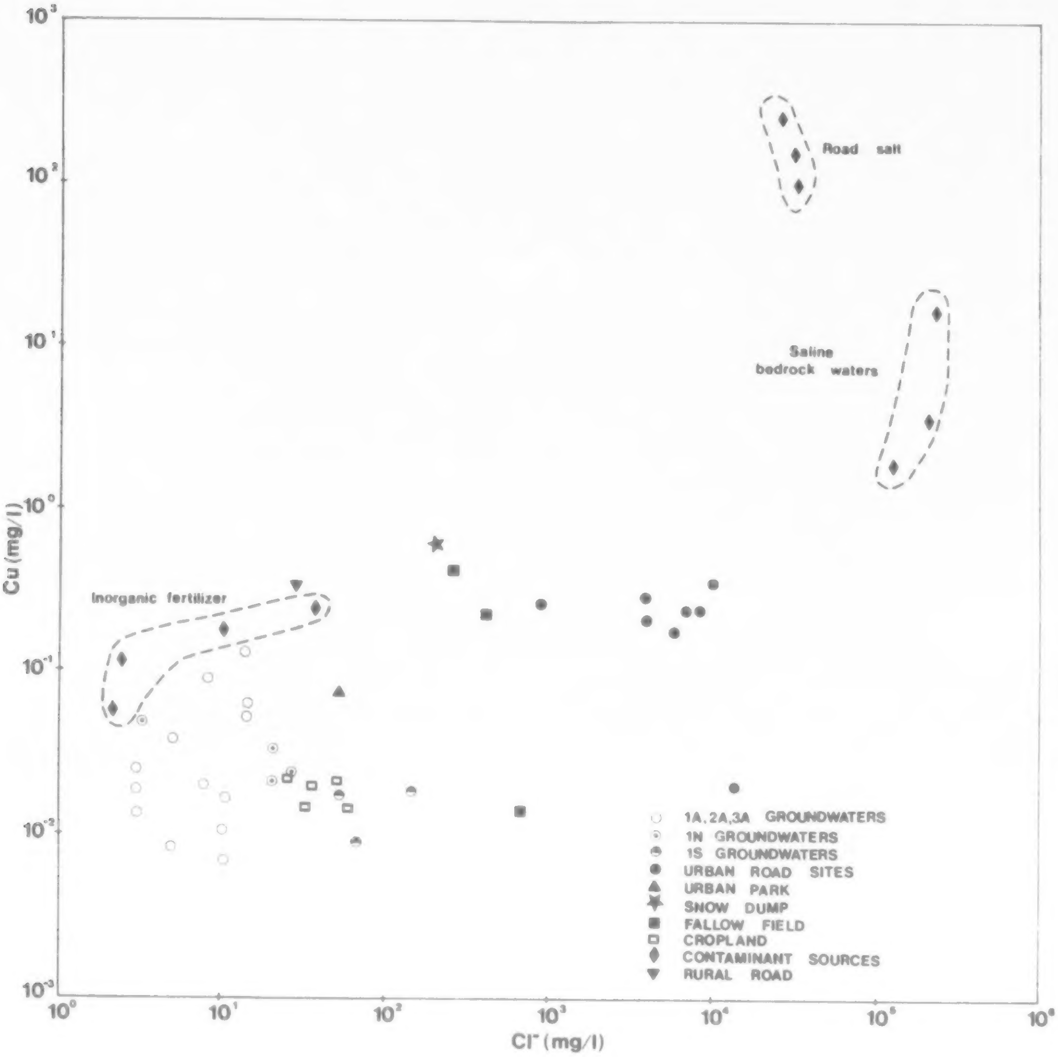


Figure 6. Plot of copper vs chloride concentration

CONCLUDING REMARKS

Shallow aquifer systems in southern Ontario frequently exhibit elevated chloride concentrations that locally exceed water quality guidelines. While in some cases the elevated chloride concentrations can be attributed to indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots.

At the University of Toronto, hydrochemical studies are in progress that aim to develop multi-parameter methods of identifying sources of groundwater contamination. Chemical parameters have included major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3) minor ions (Br, I, and F), and over 20 trace metals. To date, the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary external sources of the chloride enrichment.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. These studies have revealed very low concentrations of most trace metals in uncontaminated groundwaters, thus re-inforcing the view that trace metals have the potential to play a role in the detection and source identification of groundwater contamination. Certainly, major ion, minor ion and trace element studies of the various contaminant sources confirm the existence of chemical signatures which can definitively identify contaminant sources. However, in some cases, these signatures are modified by rock-water reactions, and more work is necessary to understand these reactions if trace metal groundwater chemistry is to be as effective as major and minor ions (particularly I and F) in revealing contaminant origins. On the basis of completed work there is good evidence that the elements Al, Ni , Ba, Cu, Zn and Pb may prove most beneficial as diagnostic indicators of contaminant origin in specific cases.

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INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:
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This part is a collation of those papers presented at Session D of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

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TRENDS IN MULTIELEMENT ANALYSIS: THE ROLE OF ICP/MS IN ENVIRONMENTAL APPLICATIONS

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I BACKGROUND

This review attempts to look at trends in multi-element analytical instrumentation in major environmental laboratories, in terms of both the forces shaping these trends and the technical instrumentation capabilities, with particular emphasis on the emerging role of plasma/mass spectrometer systems.

It is always dangerous to attempt such reviews, not only because oversimplifying generalizations are involved, but also because of the pace of change. This latter is especially true in this instance because both the pressures on environmental laboratories and instrumentation capabilities are evolving rapidly.

In overview, the needs facing the management of major environmental laboratories everywhere are simultaneously:

- increased requirements for multi-element trace component analysis at ever decreasing concentrations, sometimes with determination of the chemical form of the trace elements as well
- massive increases in sample throughput requirements, which together with the multi-element requirement produces a tremendous pressure for development of the most cost-effective strategies on a per determination basis
- unimpeachable, legally defensible data

These world-wide needs are facing major industrial laboratories just as much as those of the regulatory agencies. A financial investment review of the instrumentation industry (Ref.1) discusses the driving forces behind a generally predicted expansion rate of 25-30% per year, for instruments answering these needs, as follows.

(1) New Legislation and its Enforcement

North American examples include the U.S. Resource Conservation and Recovery Act (RCRA), $500 million of the Superfund for toxic waste analysis, and the Ontario MESA Project and Bill 309 on waste disposal. Industrial costs for compliance monitoring will be as large or larger than those of government agencies. Amendments to the U.S. Safe

Drinking Water Act are probable causes for increased monitoring of point source emission (factories) and non point (e.g., farmland). Acid rain related phenomena, with cross-boundary impacts in North America, Western Europe and Asia, are forcing legislation and measurements which are international in scope.

(2) Litigation and Liability

The enormity of toxic substance related legal settlements and/or abatement methodology costs, particularly in the U.S., but increasingly world-wide, is putting a premium on legally defensible unimpeachable analytic data, and plenty of it. This applies both on the industrial side in proving compliance and on the regulatory agency side, in documenting site emission.

(3) Emerging Public and Consumer Attitudes

An increasingly knowledgeable and pollution-conscious public creates a demand for information on trace toxic chemicals in food, air, water, foodstuff and manufactured goods.

(4) Process Control and Monitoring

The trend toward higher technology industrial development, such as the semiconductor and biotechnology sectors, is generating a concomitant need for approved trace chemical analysis, driven by impact awareness in both directions. For example, impurities in input water and air have costly adverse effects on integrated circuit manufacture and fine chemical production, both growth areas. Conversely, silicon valley companies have already spent over $100 million on toxic chemical storage clean-up and workplace monitoring.

It seems clear that these driving forces are now being amplified by a very positive mutual feed-back effect. Available analytical instrument capabilities and the already available data from them are beginning to paint a clearer picture in many environmental, occupational and industrial areas internationally, and this ability to translate the trace chemical environment into a visible picture is a widely perceived technical reality. Termed the Rosetta stone effect, the demand for the analytical instrumentation to provide more and more translations of the complex chemical messages in the total planetary ecosphere is growing inexorably.

Much of the data which has had broad societal impact, such as the blood lead level in human population groups or the mercury in fish or in bottom sediments in river systems, has been obtained to date at natural bio-accumulator points in the total system. Increasingly, attention is turning to documentation of pathways on both a macro and micro scale, not only to obtain a better scientific understanding of the transport phenomena involved and hence true cause and effect, but also to provide unassailable documentation for political, legal, industrial or public action. For the analyst, pathways such as acid rain, rivers, aquifers, drinking water, urban air and dust, estuarial waters involve much lower concentrations of the trace elements of interest - typically sub parts per billion (or sub nanograms per gram) which not only push instrumentation capabilities to the present limits but equally demand of analytical laboratory operators unprecedented standards in sample collection, handling, laboratory cleanliness and verification of data.

There is increased awareness of the importance of knowing the chemical forms in which the element is present in the environmental sample. For example, tetra ethyl lead or alkyl mercury are not only orders-of-magnitude more toxic than the elemental forms, but also the transport and accumulation mechanisms are dramatically different. Thus another emerging challenge is to provide analytical capability for chemical form determination at the trace level.

The next section briefly reviews the present multielement analytical instrumentation situation, and particularly attempts to place the emerging role of plasma/mass spectrometer instruments into the perspective of the foregoing admittedly dangerous generalizations.

II MULTIELEMENTAL ANALYSIS INSTRUMENTS: THE PRESENT AND EMERGING PLAYERS

Since there have been a number of excellent recent reviews of specific instruments, it seems most appropriate to summarize briefly, citing from those reviews and focussing on the environmentally important aspects.

A well-equipped environmental multielement laboratory today will probably have as major instruments:

- energy and wavelength dispersive X-ray fluorescence spectrometers

- flame and/or graphite furnace atomic absorption optical spectrometers (AAS)

- plasma (likely inductively coupled) atomic emission spectrometers (ICP/MS)

and some will have, in addition to these x-ray and optical instruments, the relatively new

- inductively coupled plasma/mass spectrometers (ICP/MS)

Additionally, some laboratories may have access to neutron activation analysis capabilities. This is a powerful technique but not generally available and will not be covered in this review of instruments.

X-Ray Fluorescence Spectrometers

X-Ray instruments utilize a closed x-ray excitation source and a closed detector to provide both energy and wavelength dispersive data from which absolute amounts of various elements in the sample can be determined (Ref.2). First introduced commercially in the 1950's and 60's by instrument companies such as Philips, Siemens, Analytical Research Laboratories, Rigaku and Kevex, they are by now highly developed, reliable and stable instruments. Although relatively expensive, with modern computer-controlled acquisition, manipulation and presentation of data they rate highly on sample throughput and cost per determination scales, and provide reliable data.

Unfortunately, the physical limitations imposed by the brightness of available x-ray sources, the necessary source-sample-detector geometries, and detector sensitivities all place detection limits typically in the micrograms (or parts per million for a gram sample) range, and worse for low z elements. Because of the limited penetration power of the x-rays, they also tend to be limited to near-surface analysis, making them particularly well-suited for some forms of sample, such as filter-collected airborne dusts. With these limitations in mind however, they deserve careful consideration in planning environmental laboratory protocols for major sample processing campaigns, in that they provide reliable determinations of major and minor sample analytes, particularly useful in a pre-screening role before subsequent trace analysis by other instruments.

The precision and accuracy of the signals they produce are statistically limited, and since these instruments are relatively mature in their development cycle, there does not seem to be a reasonable expectation of major improvements in sensitivity and detection limits.

Flame and Furnace Atomic Absorption Instruments

Although they are not strictly speaking fully multielemental in practical terms, the acceptance and rapid growth in use of first flame and later furnace atomic absorption instruments has led to their use in many multielement environmental applications. The combination of reasonable capital costs and picogram-level detection limits (with furnace AA) for many elements is part of the reason. These instruments have EPA approval.

AAS instruments utilize an atomizer source (flame or furnace) to convert at least some of the sample into dissociated atoms in the source. Light from a radiation source for the element of interest is passed through the flame and is attenuated by resonant absorption proportional to the concentration (Ref.3). Commercial instruments are available from Varian, Perkin-Elmer, Thermo-Jarrel-Ash and other firms. Linear response ranges are not very large - typically approaching two orders-of-magnitude, so care must be taken with analyte loadings.

It is geometrically practical to provide up to six lamps for sequential multielement analysis. With the present highly developed automation of these flame AA instruments, 85 samples per hour can be analysed for six elements each, or about 500 determinations per hour. (Ref.4).

Flames are poor dissociators for the more refractory elements and the alkaline earths. Also, elements with their resonance lines in the far ultra violet such as the halogens, sulphur and phosphorous are not easily determined, with conventional commercial instruments.

Compared to flames, graphite furnaces provide up to 1000 times better detection limits. Although initially plagued with major interference effects, these have now been commercially developed, through better furnace technology, better photometric design and the elegant use of the Zeeman effect to reduce background interference. Both flame and furnace AA tend to suffer from chemical matrix problems related to volatilization and dissociation effects in the flame or furnace, while the ICP optical systems discussed below have much less problems in this area but do have problems from the overlap of atomic emission spectra.

A simultaneous multielemental AA system using a continuum source, initially studied by O'Haver, termed SIMAAC, has been under laboratory development for several years (Ref.5), but is not commercially available. Based on graphite furnace atomization, even with the Xenon-lamp continuum source brightnesses presently available it offers superior detection limits for many elements, and seems less susceptible to cross-compound optical spectral interferences than the optical systems discussed below. Unfortunately, lamp brightnesses fall off drastically in the far ultraviolet so elements absorbing in this region are poorly detected.

Although research groups have studied the possibility of utilizing atomic fluorescence (rather than absorption) in the form of simultaneous multilamp, multielement furnace atomic fluorescence (Ref.6) no commercial instruments have yet appeared.

Plasma Emission Instruments

The most highly developed truly multielemental trace analysis systems today are based on measuring the optical emission spectra of atoms or ions either from a DC arc or from an induction coupled plasma tail-flame (ICP/AES). While DC arc-based systems are in wide-spread use in industrial laboratories, environmental laboratories have tended to utilize predominantly instruments based on induction coupled plasmas. Multiple detectors can be arrayed along the focal plane of the spectrometer for simultaneous determinations of up to 60 elements, utilizing optimally selected emission lines to help minimize cross-element spectral interferences. Background correction can be provided by scanning to obtain a measure of the background signal near the lines of interest. Alternatively, a fast scanning sequential monochromator mode may be used. Marketed by companies such as Perkin-Elmer, ARL, and Thermo-Jarrel-Ash, these systems are highly automated and computerized. 40 to 50 elements per minute or 3000 determinations per hour can be achieved on the Perkin-Elmer instrument. Ultimate detection limits are not as good as graphite furnace AA, typically being in the low to mid parts per billion range, with refractory metals, arsenic, lead, selenium and other heavy metals of particular interest environmentally being detected with least sensitivity.

At their present state of development these systems have a signal stability of better than 1% per hour. Determinations to 1% precision can be made, with perhaps 1% accuracy if recalibrated every 2 hours with a similar matrix calibration solution.

Plasma/Mass Spectrometer Instruments

The induction coupled plasma also can be used as a mass spectrometer ion source. Instead of utilizing optical emission or absorption from atoms and ions, elemental ions from the plasma tail flame are extracted into a mass spectrometer for analysis via a mass spectrum. In the six years since the first paper was published (Ref.7), there has been rapid growth in the technique with two commercial instruments introduced - by SCIEX® Division of MDS Health Group Limited in Canada in 1983 and V.G. Isotopes in England in 1984. Basically, this growth occurred because this approach seemed to offer three simultaneous advances over optical multielemental analysis instruments - improved detection limits over the complete periodic table of elements, a spectral simplicity which could in principle, vastly reduce spectral interference problems, and the intrinsic capability of providing isotopic abundance data along with multielemental analysis.

Reviews of ICP/MS were published in 1985 (Refs.8, 9), but there has been very considerable progress made in improving key performance parameters since then, which this review will attempt to summarize.

The basic principle of operation of an ICP/MS system can be understood from Fig. 1, and more detail is provided in Refs. 8 and 9. Most commonly, solutions to be analysed are sprayed into a conventional atmospheric pressure ICP using a nebulizer, but it is obvious that many alternative methodologies for sample introduction can be applied. Under typical sample loading and powers, most elements in the periodic table are highly ionized in the ICP.

Gasdynamic beam techniques utilizing a two stage expansion through conical orifices then extract the center line flow of the plasma tail flame into a vacuum region housing a quadrupole ion filter, which can be rapidly scanned electronically to provide a complete mass spectrum or can be used in a rapid peak-hopping mode to monitor only selected elemental ions.

The usual ion sampling position in the plasma tail flame is approximately the same as the viewing region in the optical systems. The instantaneous signal is proportional to the centre line ion flux crossing the sampling orifice rather than the instantaneous integrated concentration of atoms and ions (depending on the emission lines selected) in the viewing region of an optical system, but these signals are very closely related. This correlation has been closely documented in a paper by Gillson (Ref.11), using simultaneous optical and mass spectrometric sampling of the plasma tail-flame. Thus, while the basic spectral line interference situation for ICP/MS is vastly simpler than for ICP/AES, and detection limits better, the chemical plasma matrix interference effects should be fundamentally almost identical for the two systems.

Many studies have shown that the ICP is relatively free from chemical matrix interference effects compared to flame and furnace AA, due to the high degree of dissociation and ionization of the analytes, an important attribute for achieving wide linear dynamic response range and true multielement analysis capability. However, high plasma loadings either from large nebulizer liquid flow rates or high inorganic matrix content (such as high salt content) can load the plasma so that the instrument sensitivity for individual elements can be affected. This applies to both ICP/AES and ICP/MS systems.

Under typical ICP conditions of about 8000°K and 1 atm pressure, the sample will be a dense plasma containing about 10^{15} total ions and elecrons per cm^3, dominated by the reagent argon carrier ions and with ionic populations of the analytes proportional to their concentrations. It turns out that in this plasma there will also be, at very much lower levels, unwanted but inescapably present amounts of trace molecular ion species of some analytes (particularly refractory oxides) and also trace but measurable amounts of some doubly ionized species (which appear at half the nominal mass). This problem, which is primarily one of spectral interference, is however generally orders-of-magnitude less than that existing in instruments based on optical spectral emission.

The key to developing the full analytical potential of ICP/MS lay in successfully extracting this plasma through the sampling interface.

It is now clear that it is feasible to sample and retain the ionic population representative of the undisturbed plasma, because the rate of expansion is so rapid that it effectively freezes the ion population, so long as unwanted shock waves, boundary layer cooling effects and spurious electrical discharges are effectively eliminated from the central plasma expansion. This plasma sampling system was first developed by Douglas and French (Ref.10) and is incorporated in the SCIEX® ELAN® ICP/MS system.

III PERFORMANCE PARAMETER COMPARISONS

Because the ICP/MS commercial systems are in a relatively early phase of their development cycle compared to the other multielemental analysis instruments, further improvement in important operational parameters can be reasonably expected. The following discussion should be regarded as a snapshot taken at the time of writing.

Detection Limits

Detection limits in instruments are like horsepower in sports cars - often essential for the desired performance, difficult if not to say dangerous to utilize fully except in the hands of an expert, and not always the key determinant of user satisfaction in the long run.

Table 1, with portions adapted from Ref. 4, compares the present detection limits for ICP/MS (data from Ref. 12) with the other systems. As noted in Ref. 4, the furnace AA instrument provides an absolute-amount-limited response whereas the ICP (with nebulizer sample introduction) provides a concentration-limited response, and the comparison in Table 1 is made by assuming a 20 microlitre sample introduced into the furnace. This provides the picogram scale on the left. But ICP based instruments, optical or mass spectrometric, are not limited to nebulizer sample introduction. As has been recently demonstrated, the use of an electrothermal vaporizer (Ref. 13), or direct insertion probe (Ref. 14) in combination with ICP/MS can equally provide sub-nanogram level detection limits. This will prove to be of importance in many sample limited environmental studies.

The ICP/MS data show generally one to two orders of magnitude better detection limit advantage over ICP/AES, rivalling furnace AAS for many elements. Even at the present stage of development, there is particular detection limit advantage for many environmentally important elements, such as the transition metals and rare earths which are difficult to determine by other means, but of increasing importance in studying the environmental pathways for oil and coal combustion products.

The ICP/MS detection limits shown in Table 1 are those obtainable under normal operating conditions, with nebulizer uptake rate at 2 mil/min, ICP power at 1200 watts and total solid content of the analyte solution not greater than 0.2%. It is possible to improve these detection limits by factors of 5 to 10 by resorting to higher nebulizer flows, but the increased plasma loading will incur worsened matrix effects.

Response Range

While the linear response range for flame or furnace AA spans two orders of magnitude, and ICP/AES reaches between four and five, the usable response curves for ICP/MS (Fig. 2) span over 5 orders-of-magnitude. This is primarily because, with presently achieved ion extraction efficiency, the low end detection limit is generally close to the limit set by counting statistics, rather than being set by the ability of the instrument to extract the signal from a continuum or other interfering background. (The true noise background is a few counts per second). The upper limit comes from electron multiplier saturation at over 10^6 counts/sec.

This wide dynamic range helps both in initial semi-quantitative sample screening functions, and in providing better multielement analyses when trace and minor components are present in widely varying concentrations.

Signal Stability

The signal stability of an ICP/MS instrument depends obviously on the stability of operation of all parts in the system - nebulizer, plasma torch, ion extraction interface, ion quadrupole filter, lenses and detection system stability. In comparison with ICP/AES systems, the key differential area in determining relative stability is the ion sampling interface, since modern ion filtering and detection systems have very good stability. The stability possible at the present state of development of one commercial system, the SCIEX® ELAN®, has been reviewed by Douglas (Ref. 15). Taken from this reference, Fig. 3 shows the raw ion count rates for elements, each present at 100 nanograms per millitre, measured over 13 hours. It is seen that there is a drift of 1-2% per hour. Most elements drift in the same direction which means that an internal standardization can be readily applied to correct much of this drift. Fig. 4 shows that, with the addition of one mid mass range internal standard (in this case rhenium) a stability of ± 1% over six hours is obtained. This compares well with good ICP/AES systems, leading to the important conclusion that ion sampling interfacing can be achieved without introducing additional drift, for solutions of this dilution.

However, for a refractory matrix of salt content of 0.1% or greater an additional source of drift can be encountered which is apparently due to gradual salt deposition on the sampler or skimmer cones. Fig. 5 shows the stability obtained for 6 elements at 100 nanograms/millitre in 2000 parts per million uranium salt solution. Despite the high salt content, signals decreased by less than 10% over 8 hours.

In the reviewer's opinion, this salting artifact should not be viewed as a fundamental limitation of the ICP/MS system. Rather, it is encouraging that this level of stability has been achieved so soon in the overall development. It is quite possible, with the development of more refractory skimmers and samplers, that operation at higher temperature (reduced cooling) will in future eliminate this salting problem. This could be a minor modification to existing systems.

Matrix Effects

These remarks apply equally to a second phenomena, also discussed in Ref. 15. At the present stage of development of ICP/MS technology, there can be signal suppresions varying between 0 to 50% for salt content of the order of 0.1% (1000 ppm). This suppresion effect, which is more severe than that observed in ICP/AES instruments, is generally worse at higher plasma sample loadings and is mitigated with light loadings. The cross-element interferences are generally mass dependent.

Higher salt content than 0.1% can be run provided the analyst uses careful matched matrix calibration to compensate. The method of standard additions is very helpful. However, limiting the total solid content to 0.1% is generally recommended as more straight forward at present. While this is lower than the tolerable levels in ICP/AES, the superior detection limits offer compensation.

This effect, obviously greater than the matrix effects in the plasma flame well-documented by ICP/AES users, is by inference related to the ion sampling process, and is not well understood at present. Again, there are no reasons to expect that this is fundamental, and improvement can be reasonably expected as the basis of the phenomena becomes better understood.

In the meantime however, it has already been demonstrated by McLaren, Beauchemin and Berman (Ref. 26) that the isotope dilution technique (see below) available with ICP/MS can be used successfully to eliminate matrix suppresion errors and thus permit analysis of more concentrated solutions.

Possible Spectral Interferences

There can be occasional spectral interference in ICP/MS from isobaric ions which can cause difficulties with specific ions. As mentioned above, the plasma at 8000°K can contain small amounts of doubly charged ions and refractory metal oxides, depending on the sample matrix (Ref. 16). Also, if acids other than nitric are used in sample work-up, molecular ions of the acid species have been observed and can interfere. A list of potential interferences has been provided by Vaughn and Horlick (Ref. 17). Besides nitric acid digestion, McLaren and co-workers have discussed useful alternate sample preparation processes developed to minimize ICP/MS molecular ion interferences (Ref. 18). In general, these spectral interference effects are small compared to the situation in ICP/AES instruments, but they can be troublesome in some specific element/matrix situations.

Isotope Ratio Determination Capability

This capability, effectively unique to mass-spectrometer-based instruments, depends on several instrument parameters. The precision achievable for each isotope is determined in the limit by counting statistics, but sometimes more dominant noise sources can be present such as plasma flicker due to nebulizer spray droplet statistics. Accuracy can be affected by the abundance ratio capability, a spectral resolution number which describes the degree to which the tail of adjacent mass peaks overlap into the central region of the ion being measured. This abundance ratio is less than 10^{-6}(Ref.19), meaning that an isotope can be determined even in a matrix which presents adjacent mass ions one million times in excess.

Data contained in Ref. 15 illustrate the achievable accuracies possible at present using peak hopping to help average out plasma flicker noise. With silver at 1.0 microgran/millitre, the $^{109}Ag^+/^{107}Ag^+$ ratio was determined to be ± 0.06%. This is a favourable case because the isotope abundance ratio is close to unity. For a less favourable case, strontium $^{87}Sr^+ \div ^{88}Sr^+$, the data indicate .08% precision was achieved for a ratio of .086. An error of 1 to 2% compared to the actual ratio comes from a well-known mass discrimination bias across the mass range; when a correction factor is applied by calibrating with a certified isotope ratio solution, the determined ratios in test cases agree with known values to within the uncertainty of the experiment.

While these precisions do not match those obtainable on mass spectrometers designed solely for isotopic ratio determinations, they are nevertheless very much in the range that can be used in several ways to immense advantage in environmental work by permitting:

(1) the isotope dilution technique to be used to provide the most fundamental guarantee possible of the correctness of the absolute concentration measurements

(2) isotope ratios to be used in assisting in pollution source identification

(3) isotopically labelled isotope tracers to be used in studies of pollutant pathways, particularly in biological situations.

IV THE GROWING ROLE OF ICP/MS: ENVIRONMENTAL EXAMPLES

The driving forces on environmental needs for sample analyses previously discussed, combined with the mix of performance parameters achieved in the ICP/MS instruments to date suggest a rapidly growing role for these instruments in environmental laboratories, and an equally rapid growth in the volume of data produced. However, it is important to recall that the improvement in detection limits achieved with graphite furnace led to many papers in which the data were later found to be suspect. Claude Veillon vividly describes this situation in the story of trace chromium in biological samples (Ref. 20). With furnace AA instrumentation capable of three orders of magnitude better detection limits than previously available, standards of laboratory cleanliness and knowledge of all possible sources of trace contamination (or trace analyte loss) were not always equal to the task. Veillon suggests a "useful paranoia" in suspecting and checking every step of the analytical procedure - sample containers, transfer tubing, stopcocks, syringes, dilution and standard solutions, laboratory airborne dust, etc. While nothing is more crucial than the skill and insight of the analyst, the combination of similar detection limits together with isotopic dilution capability in the one ICP/MS instrument is a powerful help.

Isotopic dilution applied at the time the sample is initially collected also provides the best protection against error due to trace element loss in all subsequent sample handling (since these changes affect equally the unknown and the isotopically labelled spike) or changes in instrumental overall sensitivity. However, it cannot compensate for contamination, whether the source is leached from a container or from a particle of dust from the laboratory air. It should also be noted that errors can sometimes arise if the spike is not either introduced in or subsequently fully converted (equilibriated) to the same compound form as in the sample. Once again, the skill of the analyst remains the most essential ingredient.

These points are well illustrated in the recent paper by Beauchemin, McLaren et. al., (Ref. 21), on determination of trace metals in a river water reference material by ICP/MS. Quoting their conclusions directly

> "The rapid sequential multielement detection capabilities of ICP/MS combined with its good detection power give their technique enormous potential for the direct trace analysis of aqueous samples. It was indeed possible to determine fifteen elements directly in a riverine water reference material, and five more elements after a 20 to 50 fold preconcentration. This work has shown that, although analyses with external calibrations are usually more subject to errors arising from ionization interferences (caused by concomitant elements) unless the matrix of the standard solutions used to calibrate closely matches that of the samples, they can nevertheless be used

> rather efficiently in many cases, provided that an adequate correction for drift is made. The method of standard additions provides, in general, more accurate results than external calibrations as it compensates for ionization interferences. Finally, the isotope dilution technique gives by far the most accurate and precise results, but it requires two isotopes free of spectroscopic interferences, and equilibration of the spike isotope with the analyte must be achieved in order to assure their identical behaviour during any sample treatment prior to analysis."

The growing importance of ICP/MS to water sample analysis is further illustrated by the work of Taylor and Garbarino (Ref. 22) on setting up isotopic dilution ICP/MS for a program in measurement of trace metals in U.S. aquifers.

The Rosetta stone effect - the existence of trace chemical data which in turn creates a situation demanding more data - has been mentioned. Lead in the environment provides a classic example. Boeckx (Ref. 23) quotes data which show that lead blood levels in urban dwellers in the U.S. dropped from 15 to 10 micrograms per decilitre between 1977 and 1980 simultaneously with a similar percentage drop in the total tonnage of lead used in automotive gasoline. (Measurable toxic effects begin to appear in children with blood levels in excess of 10 micograms per decilitre). While cause and effect on a large scale are clearly established, the relationships in specific local situations involving multiple lead sources, such as battery factories, old paint on buildings, and lead in old plumbing pipes can be much more complex. Because the ICP/MS can determine lead at trace levels and measure its isotope ratio to help indicate the source of lead, Hinners of EPA Las Vegas has embarked on a demonstration study using ICP/MS which has shown that the sources of lead can be distinguished by this method. (Ref.24). Similar work has been initiated by Sturges (Ref.25) for lead isotopes in airborne samples in Ontario.

Another paper by McLaren and co-workers (Ref.26) demonstrates the accuracy and precision achievable using isotopic dilution ICP/MS in multielement trace analysis of marine sediments of geological interest. Table II from Ref. (26) indicates as noted in this reference that "the detection power of ICP/MS makes possible the determination of many elements for which few, if any, reliable values have been reported for geological and environmental reference materials. This increases the importance of isotopic dilution techniques in assuring the accuracy of results osbtained using other calibration strategies."

Application of ICP/MS to the study of acid rain sources, transport and effect has already begun in Ontario (Ref.27), and will be described in more detail elsewhere in this Conference Proceedings. Boomer and other researchers in the Ontario Ministry of the Environment are developing the protocols for a large-scale study of acid rain. One aspect is to provide data to help in understanding the impact of acid rain on trees, by analysing not only the trace pollutant content of the rain fall onto the forest canopy but also the altered trace concentrations on the leaf canopy, the trunk stem and in the soil and root system. Another aspect is to permit multivariant analysis to be applied in receptor modelling studies. Multielement trace analysis of received rainfall at various sites, which can contain varying ratios of pollutants injected from multiple sources, can in principle be unscrambled to determine the contribution from each source. The characteristic trace element ratios for each source will be used, but in the long run the source-specific isotopic ratios of each trace element will be of invaluable assistance in assigning the burden of responsibility to each source.

There are many other examples of potential large scale environmental application of ICP/MS under consideration, including particularly drinking water analysis. Many of these will require, as is appropriate, extensive developmental testing before receiving regulatory agency approval. It is already clear however, as these early examples perhaps suggest, that ICP/MS will play a large role in this area in future.

TRENDS, INCLUDING THE CARE AND FEEDING OF SAMPLES

As noted, the increased detection limit capability of ICP/MS brings concomitant need for care in sample collection, handling and work-up. But the sheer volume of samples, together with the diversity of sample forms and matrices of environmental importance, is pushing development in the feeding of samples - more versatility, convenience and efficiency in the methodologies which feed the samples into the instrument. Velmer Fassel (Ref. 28) believes that there will be further innovations and improvements in sample introduction techniques beneficial to all ICP-based instruments, including improved ultrasonic nebulization with aerosol desolvation, direct injection combined with hydride formation, ICP/MS utilized as an element - specific detector for liquid and gas chromatographic effluents, and direct aerosol injection from solids. This reviewer concurs, and would even extend the list, for there are many examples of this trend in the recent literature. First, the electrothermal vaporizer (ETV) has been combined with ICP/MS by Park et al. (Ref.13) in an improved geometry which provided over 80% transfer efficiency of the microsample into the ICP torch and indicated nanogram per gram range detection limits. In an equally promising alternate approach Boomer and Powell (Ref.14) have reported excellent results for microsamples inserted directly into the plasma on a refractory metal loop probe. Ultimately, ease of automation and flexibility of operation to permit staged drying, ashing and chemical matrix modification as desirable will be important.

The use of laser surface ablation combined with ICP/MS has been reported by Arrowsmith (Ref.29). Indicated detection limits are in the low nanogram per gram range. Besides the excellent sensitivity of this approach, it is noteworthy that, in an operating mode in which the laser is free-running and is rastered across the sample face, it offers the potential for direct homogenized multielement determination for the sample face, without the need for intermediate sample dissolution and work-up. This appears particularly attractive for filter-collected samples, for example.

Of particular interest to the biologically oriented aspects of environmental studies, the first papers reporting on gas chromatographic interfacing with ICP/MS have appeared. Van Loon et. al., (Ref.30) have directly connected a gas chromatograph to the ICP torch and using three pentylated tin compounds have reported results which suggest that for compounds which can be derivatized into a form suitable for the gas chromatograph, heavy metal specification of organic samples shall be feasible with high picogram range detection limits. In another study by Chong and Houk (Ref.31), organic-compound-specific elemental determinations of some common elements, including their isotopic ratios were made by GC/ICP/MS for mixtures of alcohols, aromatic esters and phosphorous acid esters. Additionally, Thompson and Houk have reported the first results with reverse phase liquid chromatography coupled to ICP/MS (Ref.32) providing element and isotope specific data. These demonstrations are of particular interest to future environmental studies such as pollutant uptake in plants using isotopically labelled tracers.

This trend toward improvement and diversification of sample introduction methodologies would not be complete without mentioning the steady move toward robotics and automation applied sample handling, preparation, and introduction into the instrument. When this is combined with an integrated approach which combines the output of various instruments for data acquisition, manipulation and reporting purposes, major advances in both the sample volume throughput and in cost reduction on a per determination basis can be expected.

In summary, the trends for major environmental laboratories suggested by this reviewer are:

- a growing role for the ICP/MS instrument, both as a stand-alone instrument and integrated with other instruments in a best-available-absolute-calibration role due to its demonstrated combination of attributes - high sample volume throughput, excellent detection limits, true multielement capability, and the precision and accuracy achievable, particularly with the isotopic ratio measurement capability.
- a challenge to the environmental analyst to use all possible analytical skills, particularly care in sample handling and in improving operating conditions of environmental laboratories to the level demanded by instrumental detection limits exceeding parts per billion (nanograms per gram).
- an improvement and diversification of sample introduction methodologies, combined with increased automation computerization and integration of various laboratory instruments.

Applied wisely, these capabilities should provide the key to the cost-effective provision of the truly immense amounts of reliable environmental data which will be demanded in future.

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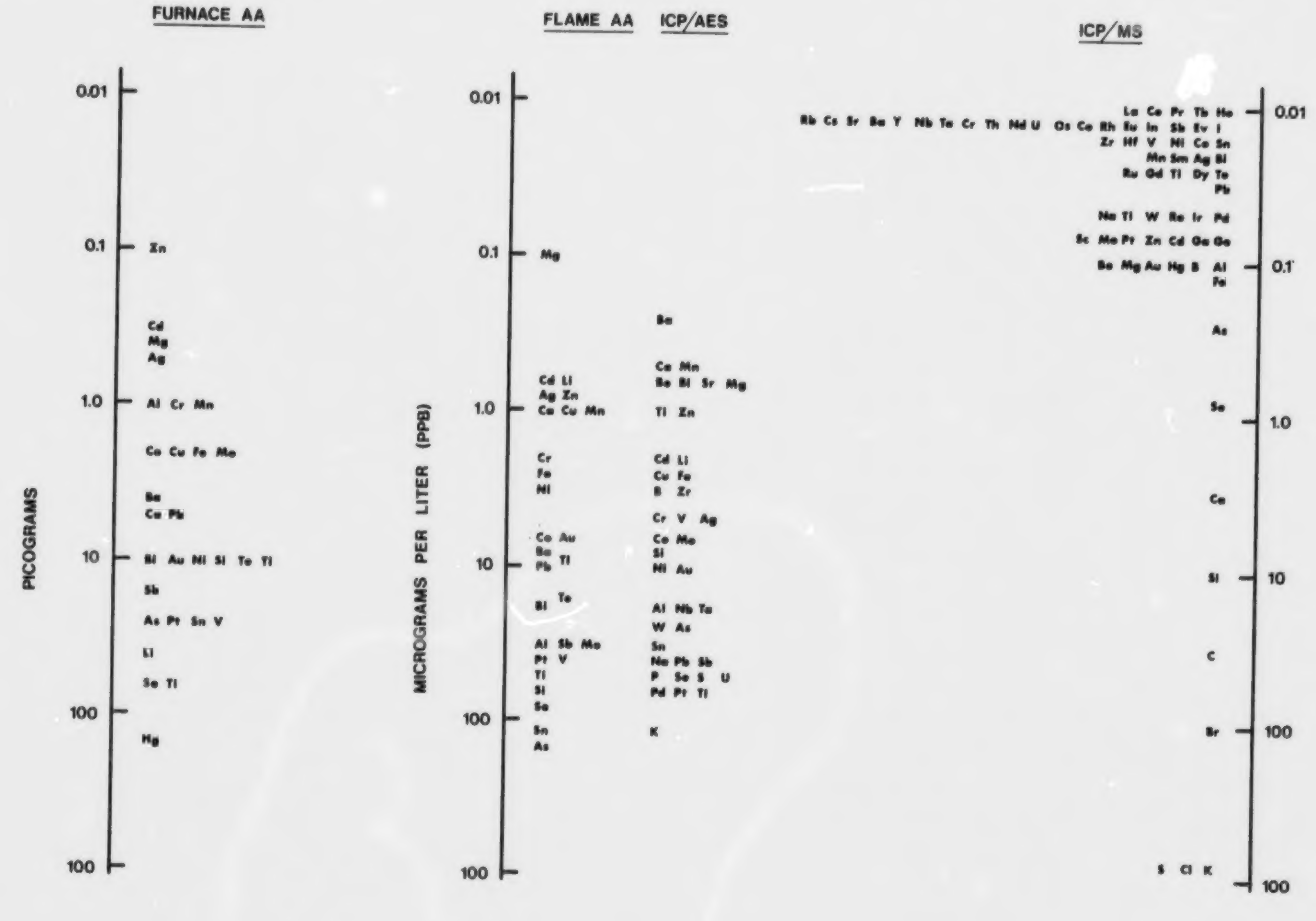


TABLE I
(from Ref. 4 & 12)

COMPARISON OF DETECTION LIMITS

TABLE II

ISOTOPE DILUTION ANALYSIS OF MARINE SEDIMENT REFERENCE MATERIALS

(from Ref. 26)

	MESS-1		BCSS-1	
Element	Found[1]	Accepted	Found[1]	Accepted
Cr	55.2 ± 0.8	71 ± 11	95.0 ± 1.2	123 ± 14
Ni	26.3 ± 0.3	29.5 ± 2.7	53.5 ± 0.6	55.3 ± 3.6
Zn	171 ± 2	191 ± 17	85 ± 4	119 ± 12
Sr	94 ± 1	(89)[5]	108 ± 2	(96)[5]
Mo	2.2 ± 0.1	(2.2 ± 0.3)[2]	2.03 ± 0.04	(1.9 ± 0.2)[2]
Cd	0.40 ± 0.03	0.59 ± 0.10	--	0.25 ± 0.04
Sn	3.8 ± 0.2	(3.4 ± 0.2)[4]	1.75 ± 0.06	(1.8 ± 0.2)[4]
Sb	0.67 ± 0.04	0.73 ± 0.08	0.47 ± 0.05	0.59 ± 0.06
Tl	0.74 ± 0.02	(0.70 ± 0.03)[2]	0.65 ± 0.03	(0.60 ± 0.05)[2]
Pb	33.1 ± 0.7	34.0 ± 6.1	22.9 ± 0.5	22.7 ± 3.4
U	4.1 ± 0.4	(4.2 ± 0.3)[3]	2.7 ± 0.2	(2.7 ± 0.2)[3]

1. Results in ug/g; precision expressed as the standard deviation (n=16).
2. Isotope dilution spark source mass spectrography with preconcentration by electrodeposition.
3. Isotope dilution spare source mass spectrography.
4. Hydride generation graphite furnace atomic absorption spectrometry. (14).
5. Flame atomic absorption spectrometry.

FIG. 1

ICP/MS SCHEMATIC

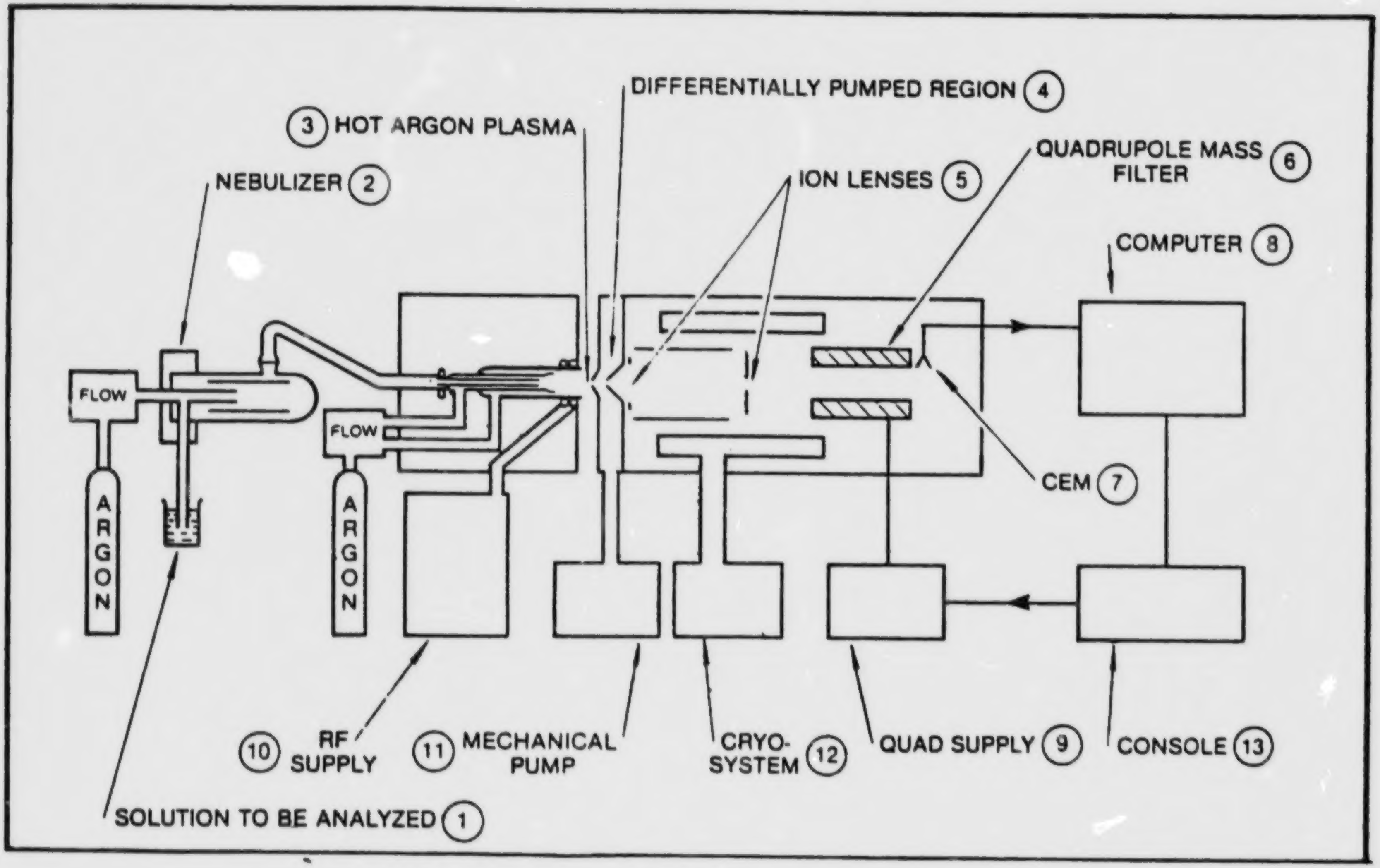
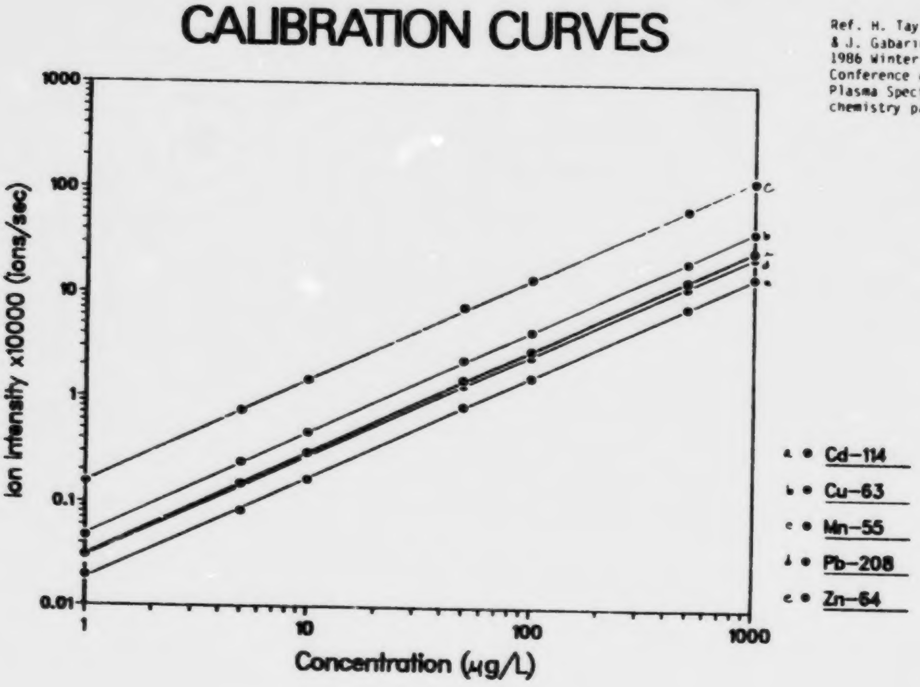
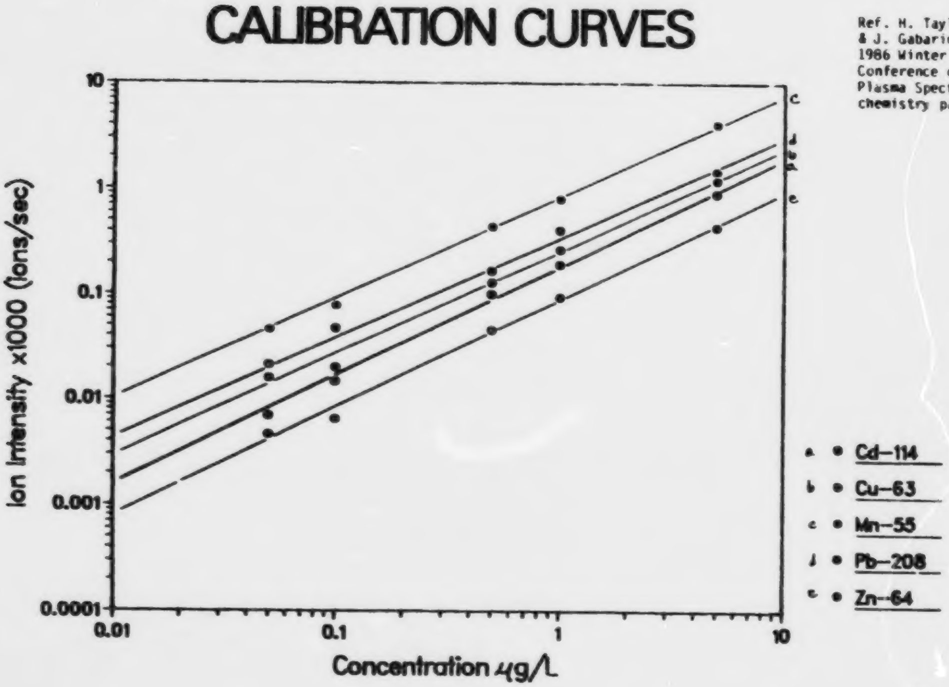

DIFFERENTIALLY PUMPED REGION ④
③ HOT ARGON PLASMA
NEBULIZER ②
ION LENSES ⑤
QUADRUPOLE MASS FILTER ⑥
COMPUTER ⑧
FLOW
FLOW
ARGON
ARGON
CEM ⑦
⑩ RF SUPPLY
⑪ MECHANICAL PUMP
CRYO-SYSTEM ⑫
QUAD SUPPLY ⑨
CONSOLE ⑬
SOLUTION TO BE ANALYZED ①

FIG. 2

TYP. ELAN CALIBRATION CURVES



Ref. H. Taylor
& J. Gabarino
1986 Winter
Conference on
Plasma Spectro-
chemistry paper #7



Ref. H. Taylor
& J. Gabarino
1986 Winter
Conference on
Plasma Spectro-
chemistry paper #7

FIG. 3 (from ref. 15)

ELAN SIGNAL STABILITY

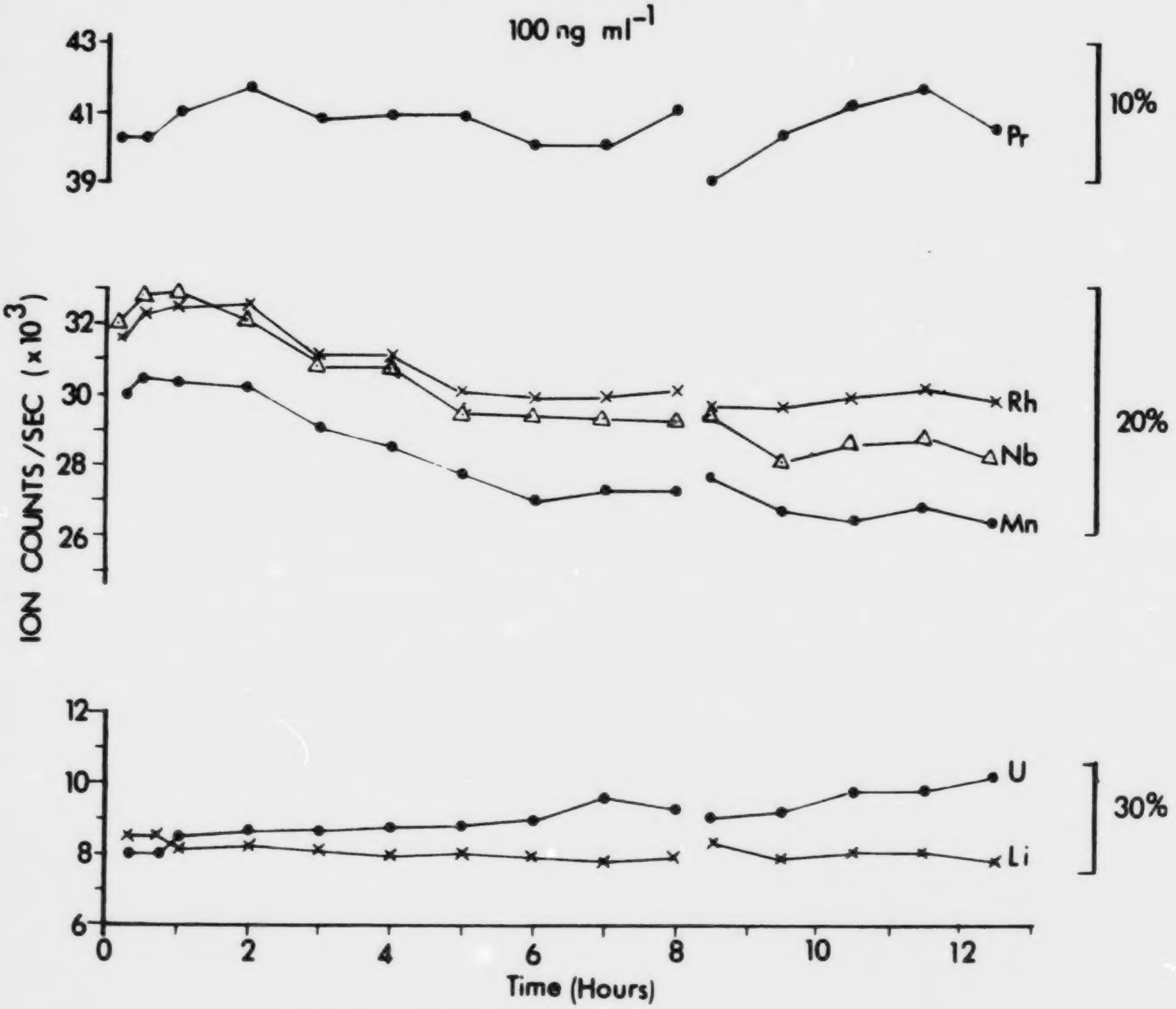


FIG. 4 (from ref. 15)

STABILITY WITH AN INTERNAL STANDARD (Nb)

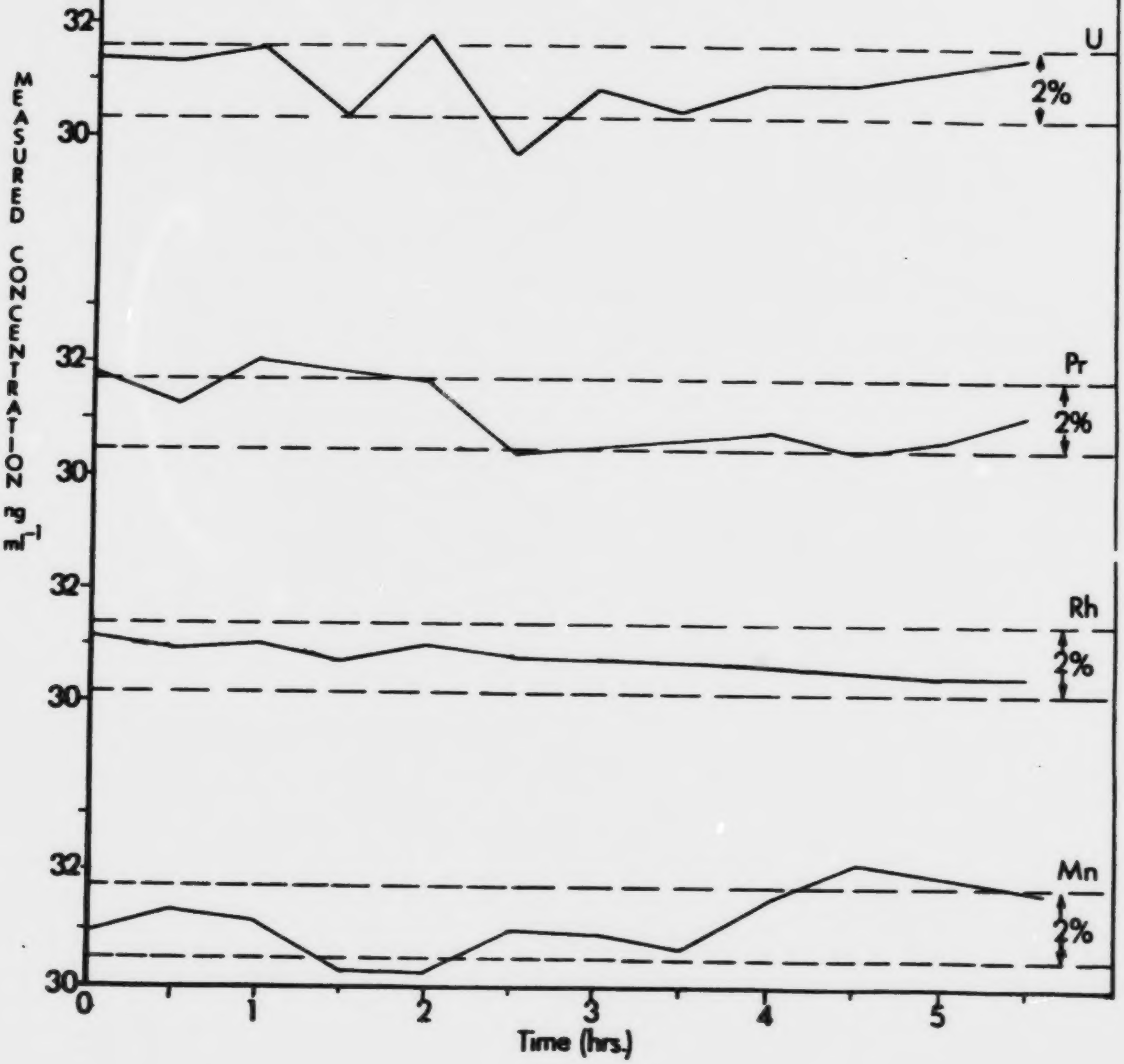
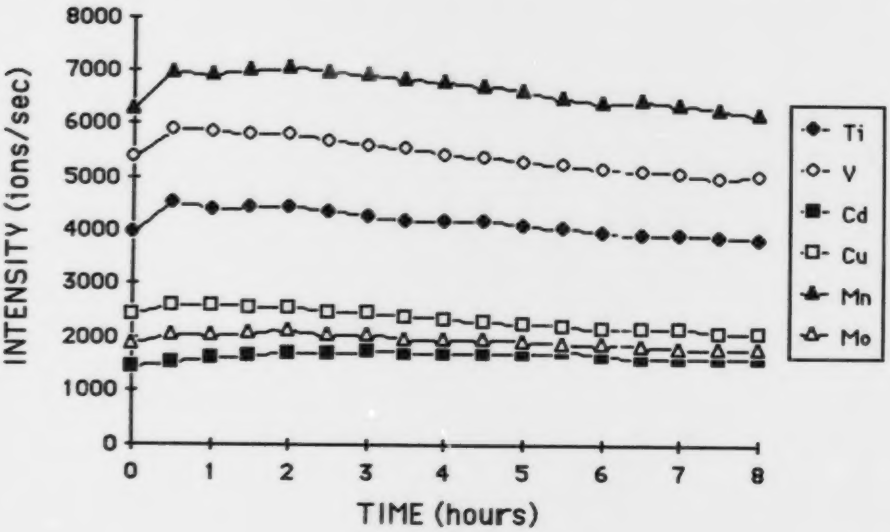


FIG. 5 (from ref. 15)

STABILITY IN THE PRESENCE OF 2000 PPM URANIUM



DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION

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Abstract

The identification of hydroxylated nitro-polynuclear aromatic hydrocarbons (OH-NO_2-PAHs) and hydroxylated nitro-polynuclear aromatic ketones (OH-NO_2-PAKs) in an ambient air particulate extract by electron impact (EI) and negative chemical ionization (NCI) high resolution gas chromatography/mass spectrometry (HRGC/MS) analyses is presented here. Bioassay-directed fractionation through three sequential separations led to detection of these OH-NO_2-PAHs/PAKs in a highly mutagenic and substantially simplified subfraction of the extract. The compound class identification was based on comparison of both EI and NCI mass spectra of reference OH-NO_2-pyrenes. The HRGC/MS retention values for nine OH-NO_2-pyrene isomers indicated that one of the compounds detected may be an OH-NO_2-fluoranthene isomer. Quantification of this compound class by NCI HRGC/MS, on-column injection, full scan acquisition, is demonstrated with sensitivity to 0.5 ng/µL.

INTRODUCTION

Urban air particles contain extractable organic matter which has both mutagenic (1) and carcinogenic (2,3) activity. Detection of the specific compounds responsible for the mutagenic activity has been limited by the complexity of these extracts and the presence of highly polar components which have been difficult to identify. To facilitate identifications, these extracts must be separated into substantially less complex fractions and analyzed with newer analytical techniques. Fractionation followed by microbial mutagenicity studies has been utilized for identifying known or suspected mutagens in cigarette smoke (4), kerosene flames (5), synfuels (6), xerographic toners (7), and diesel exhaust emissions (8,9). Bioassay-directed fractionation has been proposed (10) as the most cost and time effective approach for identification of mutagenic compounds in complex mixtures by directing the analytical and identification research effort toward only significantly mutagenic fractions. This approach should be especially useful for the detection of heretofore unknown constituents of the matrix since the methods are not directed to, or developed for, specific compounds or compound classes.

Application of this approach to ambient air particulate extracts has to date been unsuccessful in identifying major mutagenic components (11,12,13). This result seems to occur because the mixtures are substantially more complex than specific emission sources (e.g., kerosene flames) or because a major portion of the mutagenicity appears in fractions which are difficult to analyze such as the acidic and polar neutral fractions. This paper reports tentative identification of potentially mutagenic hydroxylated nitro-polynuclear aromatic hydrocarbons (OH-NO_2-PAHs) and hydroxylated nitro-polynuclear aromatic ketones (OH-NO_2-PAKs) in both a polar neutral fraction and acidic fraction of an ambient air particulate extract using bioassay-directed fractionation.

EXPERIMENTAL METHODS

Collection, Extraction, Fractionation

The air particulate sample used in this study was collected in the Philadelphia area over a two week period using a Massive Air Volume Sampler (MAVS). The operation of the MAVS has been described elsewhere in detail (14). Only particles <1.7 µm, collected on Stage III of the MAVS, were used for this study.

A 49.1 g sample of the air particles was extracted using a Soxhlet apparatus under yellow fluorescent lights for 24 hours with a 300 mL volume of methylene chloride and then for 6 hours with a second 300 mL volume of methylene chloride (Burdick and Jackson, Distilled-in-Glass quality).

An overview of the total fractionation scheme which resulted in analysis of one mutagenic subfraction is shown in Figure 1. The sequential path taken for this research effort is indicated in boldface and is described below. The first level of fractionation was applied to the methylene chloride particulate extract. This separation, involving acid/base partitioning and open bed silica gel column chromatography, has been described in detail elsewhere (15). The elution solvents of the silica gel correspond to the designation of the five fractions collected. These five fractions represent the general compound classes of aliphatic hydrocarbons, aromatic hydrocarbons, moderately polar, highly polar and extremely polar neutral compounds.

The second and third levels of fractionation were achieved using normal phase high performance liquid chromatography (HPLC) (Zorbax SiO_2, 4.6 mm x 25 cm column, Dupont Instrument Co.). The HPLC system was assembled from modular components consisting of an Altex Model 430 gradient programmer with Model 100A pumps (Altex-Beckman Co.) and an LDC Model 1203 UV detector (Laboratory Data Control Co.). A flow rate of 1 mL/min was used. The eluate was monitored for UV absorbance at 254 nm.

The second level of separation, applied to the methylene chloride silica gel fraction (CH_2Cl_2), was achieved by HPLC using a linear gradient of methanol:methylene chloride (2:98, v:v) in hexane. The gradient was initiated with 8 percent of the methanol:methylene chloride mixture and increased to 35 percent over 30 minutes.

The third level of separation, applied to the third subfraction of the methylene chloride fraction (CH_2Cl_2-C), was achieved using a linear gradient of 80 percent methylene chloride in hexane increasig to 100 percent methylene chloride in 30 minutes.

Mass Spectrometry Methods

Mass spectra were recorded using a Finnigan Model 4500 mass spectrometer equipped with an electron impact (EI) chemical ionization (CI) source. For EI analyses, a 70 eV electron beam, emission current of 0.3 mA, and an ion source temperature of 180°C were used. For negative chemical ionization (NCI) analyses, methane was used as the reagent gas at an indicated ion source pressure of 1.0 torr. Methane was ionized by a 150 eV electron beam and the source temperature was maintained at 180°C. Data acquisition was controlled by a Finnigan INCOS Model 2100 data system. A scan rate of 1 second per scan was used for both the EI and NCI analyses. The scan range was 80-450 amu for the EI analyses and 100-450 amu for the NCI analyses.

High resolution gas chromatography (HRGC) for the EI- and NCI-MS analyses was achieved using a Hewlett-Packard Ultra #2 fused silica capillary column (5 percent phenylmethylsilicone bonded phase, 50M x 0.31 mm ID, 0.52 µm film thickness) with methane carrier gas (linear flow velocity of ~75 cm/sec at 40°C). The GC column was interfaced directly to the ion source of the mass spectrometer. On-column injection at 38°C was used. For the EI HRGC/MS analyses, the column temperature was held at 38°C for 2 minutes, programmed ballistically to 100°C in 3 minutes, and programmed 100-320°C at 8°C/minute. For the NCI HRGC/MS analyses, the column temperature was held at 38°C for 0.5 minute, programmed ballistically to 150°C in 3 minutes, and then programmed 150-320°C at 10°C/minute.

Quantification was performed using D9-1-NO_2-pyrene (D9-NP) as the internal standard at a concentration of 2.5 ng/µL. The analyses were performed using on-column injection NCI HRGC/MS with instrumental conditions as described above. The calibration standards covered a 100 fold concentration range.

Chemicals

Reference OH-NO_2-pyrene isomers, 1-NO_2-3-,4-,5-,6-,8-,9-, and 10-OH-pyrene, were obtained from L. M. Ball. The synthesis and characterization of these isomers have been detailed elsewhere (16). Reference 1-NO_2-2-OH-pyrene was obtained from A. Greenberg and 1-NO_2-2-OH-fluoranthene was obtained from B. Zielinska. For the sake of clarity in discussing these isomers, the OH functional group will be listed first, despite conventional nomenclature, since the NO_2 substituent retains position #1 throughout these discussions.

Distribution and Recovery Studies

Reagent spikes in methylene chloride of 3-OH-1-NO_2-pyrene (3-HNP, 12 µg) and mixed 6-OH-1-NO_2- and 8-OH-1-NO_2-pyrene (6/8-HNP, 106 µg) were used for distribution and recovery studies. The first three steps of the fractionation scheme (i.e. acid/base partitioning, silica gel column chromatography, and the second level of fractionation HPLC method) were evaluated separately, each in duplicate. Two of the three fractions resulting from acid/base partitioning, acidic and neutral component fractions, were analyzed. Three of the four silica gel column chromatography fractions, hexane:benzene, methylene chloride, and methanol, were analyzed. For the HPLC method of the second level of fractionation, the HNP were injected and the retention window 31-39 minutes, which encompasses elution of 3-, 6-, 8-HNP, was collected and analyzed. Recovery through the third level of fractionation was estimated by taking the average UV response (n=3) for each compound analyzed by the third level HPLC method, dividing by the average UV response of each compound analyzed by the second level HPLC method and multiplying by recovery determined above for the second level method. For this study 10 ng of 3-HNP and 30 ng of 6/8-HNP were analyzed each time.

The recovery was also determined for reagent and matrix spikes of 3-HNP (12 µg) and 6/8-HNP (106 µg) in which acid/base partitioning was followed by isolation of the HNP in the acid fraction using the HPLC method of the second level of fractionation. Following injection of the acid fraction, the HPLC retention window 31-39 minutes was collected and analyzed. The methylene chloride extract of the NBS Standard Reference Material 1649 (Washington, D.C. Urban Air Particulate Matter) was used as the matrix material.

Microbial Mutagenicity Methods

The organic extracts and fractions were assayed for mutagenicity toward Salmonella typhimurium strain TA98 with and without exogenous metabolic activation (+S9,-S9) in the Ames plate incorporation assay (17). Minor modifications to this protocol, including the minimal histidine in the base agar and incubation of the plates for 72 hours, have been described in detail elsewhere (18). The plates were counted electronically using an Artek Model 880 automatic colony counter. The studies reported here for TA98 included positive controls both with activation (2-anthramine) and without activation (2-nitrofluorene). Non-linear model slopes were determined from the dose response data (19).

Samples from the first level of fractionation were tested with and without S9 at seven doses with triplicate plates at each dose. Samples from the second level of fractionation were tested with S9 at 3-9 doses with single plates at each dose. Samples from the third level of fractionation were tested with S9 at a single dose in the range of 1-50 µg depending on available sample quantity.

RESULTS AND DISCUSSION

Rationale for Comparing EI and NCI HRGC/MS Analysis Results

To determine whether a complex fraction had been reduced in components to a relatively small number of potential mutagens, the results of EI and NCI HRGC/MS analyses of a fraction were compared. This comparison was used initially to determine whether additional fractionation was required. Further fractionation was not required if (1) individual HRGC/MS chromatographic peaks contained a single component, and (2) the same set of compounds were detected in both EI and NCI analyses. The latter criterion was chosen on the assumption that polar ambient air mutagens, like nitro-PAHs, may be electronegative and present at low concentration levels in the original extract. While EI ionization provides approximately equal ionization efficiency, and hence detection, for all compound classes, NCI greatly favors ionization, and hence detection, of electronegative compounds. If fractionation has substantially reduced the complexity of a subfraction, detection of compounds by both MS techniques may provide reasonable assurance that the significant low level electronegative components of the subfraction have been detected.

After sufficient fractionation, comparisons of EI and NCI mass spectral data were used to select the potentially mutagenic compounds. Ambient air particulate extracts are clearly too complex for sequential fractionation to provide single component subfractions. Our approach was to use sequential fractionation to generate multi-component subfractions and then to rely on the separation powers of HRGC/MS to provide single component identification. The rationale for selecting the potentially mutagenic species in multi-component subfractions was based on the observation that many chemically reactive and mutagenic compounds (e.g., cyclopenta[cd]pyrene, benzo[a]pyrene, 1-nitropyrene) have a higher response under NCI MS conditions than under EI MS conditions. In this work, comparison of EI and NCI HRGC/MS analysis results has been used to identify as potential mutagens those components which exhibit higher response under the NCI conditions than under EI conditions.

Distribution of Mutagenicity for the First Level of Fractionation

The distribution of direct (-S9) and indirect (+S9) acting mutagenic activity among the seven compound class fractions of this separation are given in Table I. A mutagenicity enrichment factor (MEF), defined here as percent activity divided by percent mass, is also shown for these fractions. The CH_2Cl_2 fraction had a relatively high MEF, 5, and nearly 50 percent of the indirect-acting activity. Analysis of this fraction by EI HRGC/MS showed two major components and ten minor components (phthalate esters, aliphatic aldehydes, aliphatic acid esters, polycyclic aromatic ketones), none of which are known to be mutagenic toward TA98. Due to the high concentration of these compounds, little, if any, other material could be detected.

Distribution of Mutagenicity for Second Level of Fractionation

Normal phase HPLC separation of the CH_2Cl_2 resulted in 86 percent mass recovery. The UV chromatogram and the percentage of recovered mass and of recovered mutagenicity of each subfraction (CH_2CL_2 -A, CH_2Cl_2-B, etc.) are shown in Figure 2. Fraction CH_2Cl_2-C contained nearly 50 percent of the recovered activity and 27 percent of the mass.

Individual peaks in the EI and NCI HRGC/MS chromatograms of CH_2Cl_2-C were relatively broad and contained at least 4-6 distinct molecular ions with overlapping fragment ion spectra. In addition, major components in the NCI analysis were not found in the EI analyses.

Distribution of Mutagenicity for Third Level of Fractionation

Although reverse phase HPLC could potentially be used to fractionate CH_2Cl_2-C, this approach was rejected since some of the mutagenic material of the fraction was not soluble in the methanol/water solvent system used. Normal phase HPLC conditions provided 85 percent mass recovery and sufficiently good peak shape and resolution to allow separation of CH_2Cl_2-C into 12 subfractions (CH_2Cl_2-C-1, etc.) as shown in Figure 3. The mutagenic activity of subfractions CH_2Cl_2-C-4 and CH_2Cl_2-C-11, 29 and 37 rev/µg, respectively, was higher than the activity of CH_2Cl_2-C. Both fractions were analyzed; results are given here for analyses of CH_2Cl_2-C-4.

Detection of OH-NO_2-PAHs and OH-NO_2-PAKs in Mutagenic Subfraction CH_2Cl_2-C-4

The complexity of the original CH_2Cl_2 fraction had been reduced such that most HRGC/MS peaks of CH_2Cl_2-C-4 contained a single component. In addition, major components in the NCI HRGC/MS analysis were also detected in the EI HRGC/MS analysis. A retention window from the EI and NCI chromatograms is expanded in Figure 4 for comparative purposes. The elution positions of two phthalate esters, butylbenzylphthalate (BBP) and di-2-ethylhexylphthalate (DEHP), were used as internal standards for relative GC retention correlation between the chromatograms. As seen in Figure 4, component 3 had a slightly different retention value in the two analyses. However, the difference in expected and actual elution time of component 3 in the NCI analysis (Figure 4) was so minor, 9 seconds, as to not affect any conclusions of this study. This difference was apparently due to the fact that although the GC phase was identical for the two analyses, the GC column itself was different.

Four OH-NO_2-PAH/PAKs, including a OH-NO_2-fluorenone isomer, a OH-NO_2-fluoranthene/pyrene isomer, and two OH-NO_2-methylfluorenone isomers, were tentatively identified in the EI and NCI mass spectral analyses of CH_2Cl_2-C-4. The OH-NO_2-fluorenone isomer was detected in both the EI and NCI analyses. The OH-NO_2-fluoranthene/pyrene isomer and two OH-NO_2-methylfluorenone isomers were detected only in the NCI analysis. The identification of component 3 of Figure 4 as OH-NO_2-fluorenone was based on the close agreement of its EI and NCI mass spectral fragmentation patterns with those of a reference OH-NO_2-PAH, 6-OH-1-NO_2-pyrene. The EI and NCI mass spectra of these two compounds are shown in figure 5. Both EI spectra show an intense molecular ion (base peak) and major fragment ions corresponding to the loss of O, NO, CNO_2 and $CONO_2$ (M-16, M-30, M-58, and M-74 amu, respectively). In addition, the OH-NO_2-fluorenone spectrum contains a fragment ion corresponding to the loss of CO (M-28). The NCI spectra of the OH-NO_2-fluorenone isomer and reference 6-OH-1-NO_2-pyrene show intense molecular ions and fragmentation ions as indicated (M-16, M-30, M-32 and M-46), which are consistent with the structure. The relative intensities of the M-30 and M-32 ions, different for these two compounds, appear to be compound and isomer specific; the ratio of intensity of M-30/M-32 ions covered a 40-fold range (0.1-4.0) in the NCI spectra of seven OH-NO_2-pyrene isomers.

Three other components, OH-NO_2-fluoranthene/pyrene and two OH-NO_2-methyl fluorenones, with NCI fragmentation identical to the OH-NO_2-fluorenone and reference 6-OH-1-NO_2-pyrene were tentatively identified. The high mutagenic activity of NO_2-fluoranthenes and NO_2-pyrenes indicated that confirmation of the identification of a OH-NO_2-fluoranthene/pyrene isomer should be pursued.

Distribution and Recovery of OH-NO_2-Pyrene Isomers Through Fractionation

Analyses of reference OH-1-NO_2-pyrene (HNP) isomers (3-, 4-, 5-, 6-, 8-, 9- and 10-OH-1-NO_2) by the HPLC methods used in the second and third levels of fractionation demonstrated that, on the basis of solubility and polarity, a OH-NO_2-fluoranthene/pyrene isomer might elute in the HPLC windows designated as CH_2Cl_2-C and CH_2Cl_2-C-4. The shaded regions of the chromatograms shown in Figure 6 correspond to the retention windows of CH_2CL_2-C (28-35 min), and CH_2Cl_2-C-4 (9-14.5 min), respectively. Four of the seven HNP isomers eluted in the CH_2Cl_2-C window and three of the seven HNP isomers eluted in the CH_2Cl_2-C-4 window.

The results of the distribution and recovery studies for 3-and 6/8-HNP in each of the steps used in isolation of CH_2Cl_2-C-4 demonstrated that a OH-NO_2-fluoranthene/pyrene isomer might be detected in a polar neutral fraction. A large percentage of the HNP (>85 percent) partitioned into the acid fraction, but a quantifiable amount remained in the neutral fraction. On 5 percent water-deactivated silica gel, these HNP eluted primarily in the methylene chloride fraction. Recovery from the silica gel HPLC column in which the mobile phase was modified with methanol was significantly better, as expected, than recovery from that column without methanol in the mobile phase. (Note: The retention windows used in these HPLC analyses correspond to elution of 3, 6 and 8-HNP, rather than to the retention windows of CH_2Cl_2-C and CH_2Cl_2-C-4.) Results of these studies are compiled in Section A of Table II.

The distribution and recovery studies showed that, although a OH-NO_2-fluoranthene/pyrene isomer could be found in a polar neutral fraction (methylene chloride silica gel fraction), a larger quantity of the compound should be detected in the organic acid fraction of the extract. Section B of Table II shows recovery results for reagent and matrix spikes of 3-HNP and 6/8-HNP in which acid/base partitioning was followed by isolation of the HNP in the organic acid fraction using the HPLC method of the second level of fractionation. By this procedure, recovery of the HNP isomers was slightly higher than 70 percent for the reagent spikes and averaged 50 percent for the matrix spikes. These results demonstrated that separation of an organic acid fraction on a silica gel HPLC column, while possibly not ideal for recovery of all fraction components, might be used to recover a quantifiable amount of a $OH-NO_2$-fluoranthene/pyrene isomer.

Quantification of HNP by NCI HRGC/MS is demonstrated in Figure 7 by the calibration curve with dynamic range of 100. The calibration curve is higher than first order in the independent variable, possibly due to decomposition mechanisms higher than first order. The molar response of 6/8-HNP relative to D_9-NP for these data, ranging from 0.74 for 50 ng of HNP to 0.10 for 0.5 ng of HNP, is higher than the molar response of 0.05 reported elsewhere (20). The relatively high response here is most likely due to our use of the cold on-column injection technique, as opposed to heated splitless injection used by the latter. Good chromatography was observed for these compounds without derivatization of the OH substituent group. Peak width at half height was 3-4 seconds and peak tailing was minimal.

Evidence for the $OH-NO_2$-Fluoranthene Identification

The organic acid fraction (Acid) of the ambient air particulate extract was separated using the HPLC method of the second level of fractionation. The retention window 28-35 minutes, that being the elution of retention window CH_2Cl_2-C, was collected, designated Acid-C, and analyzed by NCI HRGC/MS. The $OH-NO_2$-fluoranthene/pyrene isomer tentatively identified in CH_2Cl_2-C-4 was detected in this Acid-C fraction. The NCI mass spectra of this compound in both Acid and CH_2Cl_2 fractions correspond extremely well, as shown in Figure 8, and their HRGC/MS relative retentions were identical, 0.89 versus DEHP. An EI mass spectrum of this compound has not yet been obtained.

In lieu of an authentic standard at this time, evidence is presented here to support tentative identification of this compound as a $OH-NO_2$-fluoranthene isomer. First, presence in the organic acid fraction requires a molecule with a functional group such as -OH. Second, the NCI mass spectrum of this compound contains not only the $(M-O)^-$, $(M-NO)^-$, $(M-NO_2)^-$ ions, but also an ion at m/z 201 (1 percent, S/N = 10) which would correspond to $(M-O-NO_2)^-$. Third, all $OH-1-NO_2$-pyrene isomers analyzed have retention values relative to D_9-1NP which are significantly different (see Table III). The 7-HNP isomer would not be expected to elute earlier than 2-HNP. Although NO_2-fluoranthenone/pyrenone compounds are isomeric, they would not be expected in an acid fraction. Such compounds have been tentatively identified by a characteristic M-CO loss in NCI mass spectra in hexane:benzene silica gel fractions of other particulate extracts (diesel engine) with retention values relative to NP of 1.032 and 1.040 (8).

The early GC elution of this tentatively identified OH-NO_2-fluoranthene relative to the NO_2-fluoranthene isomers (see Table III) is unexpected. However, the retention order of other OH-NO_2-PAHs (see Table IV), tentatively identified in this same Acid-C fraction on the basis of their EI HRGC/MS spectra, is unexpected. For example, a OH-NO_2 -acenaphthene (MW 215) elutes earlier than a OH-NO_2-naphthalene (MW 189). Retention order may not be predicted for OH-NO_2-PAHs as readily as for PAHs (21) and NO_2-PAHs (22). For the pyrene nucleus, adjacent carbon substitution (2-OH-1-NO_2) produces the earliest eluting OH-NO_2 isomer. Substitution of fluoranthene in the bay region, 10-OH-1-NO_2, may produce a compound which through intramolecular hydrogen bonding is substantially less polar than the NO_2-PAH parent and nearly as compact in size.

Quantification of this OH-NO_2-fluoranthene isomer in the organic acid and methylene chloride extract fractions is shown in Table V. The mass distribution of this compound between these two fractions was found to be 99.7 and 0.3 percent, respectively. This distribution compares well with the distribution between acid and neutral fractions, 99.8 and 0.2 percent, respectively, determined for the reference HNP isomers in the recovery study (Table II, Section A). Calculated values for the level of this OH-NO_2-fluoranthene in the particulate extract, the MAVS Stage III particles, and in the ambient air of the site are included in Table V. For comparison, the level of 2-NO_2-fluoranthene and 1-NO_2-pyrene in this ambient air sample are shown in Table V, also.

Significance of Detection of OH-NO_2-PAHs

The presence of OH-NO_2-PAHs in particulate matter has been suggested by Löfroth, Nielsen and Schuetzle to account for mutagenicity in extract fractions more polar than those containing NO_2-PAHs (23,24,25). Similar mechanisms have been proposed by which atmospheric hydroxylation of PAHs followed by nitration readily yields both NO_2-PAHs and OH-NO_2-PAHs (24,25,26). The detection of a OH-NO_2-fluoranthene isomer in an ambient air particulate extract should not be unexpected since 2-fluoranthene has been identified and quantified in this particulate extract at 6.4 μg/g extract mass (27).

Three OH-NO_2-pyrene isomers were tentatively identified by Schuetzle (25) in diesel particle emission extracts using a tandem mass spectrometric (MS-MS) technique. Schuetzle estimated the concentration of OH-NO_2-pyrenes to be in the range of 10-100 μg/g extract. Based on the mutagenicity of a mixture of 3-, 6- and 8-OH-1-NO_2-pyrenes, the contribution to the mutagenicity of one diesel extract was estimated to be as high as 5 percent (20).

The importance of OH-NO_2-pyrenes became apparent when they were first identified as mutagenic mammalian metabolites of 1-NO_2-pyrene (16). The mutagenicity of the OH-NO_2-pyrene isomers tested (3-,4-,5-, 6-,8-,9- and 10-OH-1-NO_2) ranged from 0.06 to 8 times the activity of 1-NO_2 -pyrene (28). The OH-NO_2-pyrene isomers are generally more mutagenic in the absence of activation and appear to be metabolized *in vivo* to the corresponding ring-hydroxylated-N-acetyl-aminopyrenes, which are also mutagenic but require activation.

The higher mutagenic activity of the NO_2-fluoranthene (NF) isomers [8 NF, 42,000 rev/μg; 3 NF, 32,000; 2 NF, 2000; 1 NF, 1900 (29,30)] versus 1-NO_2-pyrene [1000 rev/μg (7)] suggests that OH-NO_2-fluoranthenes may be more mutagenic than OH-NO_2-pyrenes. The identification of both a NO_2-fluoranthene and a OH-NO_2-fluoranthene isomer in an ambient air particulate extract underscores the importance of elucidating the potential health effects of these compounds.

CONCLUSIONS

This study has demonstrated that bioassay-directed fractionation and characterization is a highly effective method for detecting and identifying heretofore unknown and potentially mutagenic constituents of an extremely complex ambient air particulate extract. Three sequential fractionation techniques of increasing chromatographic resolution produced a mutagenic subfraction that was reduced in chemical complexity such that individual HRGC/MS peaks were single components. Several OH-NO_2-PAHs/PAKs were tentatively identified in this subfraction. The identifications were based on NCI and EI mass spectra of these compounds with reference HNP and a study of distribution and recovery of HNP through the fractionation steps used. The HRGC/MS retention values for HNP isomers indicated that one of the OH-NO_2-PAHs detected in this ambient air sample may be a OH-NO_2-fluoranthene isomer. This OH-NO_2-fluoranthene isomer has been quantified in both the organic acid and moderately polar neutral silica gel fractions. Based on the levels of NO_2-PAHs in this ambient air particulate extract, the level of this tentatively identified OH-NO_2-fluoranthene is sufficiently high to suggest that if mutagenic, this compound may help account for mutagenicity in polar fractions.

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TABLE I. DISTRIBUTION OF MASS AND MUTAGENIC ACTIVITY FOR FIRST LEVEL OF FRACTIONATION

		Mutagenic Activity,(a)			
		-S9(c)		+S9(d)	
Fraction	Mass, %(b)	%(e)	MEF(f)	%	MEF
Organic Acids	7	38	5.4	21	3.0
Organic Bases	1	1	1.0	1	1.0
Hexane	21	0	0.0	0	0.0
Hexane:Benzene	14	8	0.6	12	0.9
Methylene Chloride	9	23	2.6	45	5.0
Methanol	34	29	0.9	21	0.6
Acidic Methanol	14	1	<0.1	<1	<0.1

(a) Mutagenic activity toward Salmonella typhimurium TA98.
(b) Mass recovery, 94% (15).
(c) Direct acting mutagenic activity recovery, 84% (15).
(d) Indirect acting mutagenic activity recovery, 88% (15).
(e) Percent distribution of recovered activity
(f) Mutagenicity enrichment factor: % activity divided by % mass.

TABLE II. DISTRIBUTION AND RECOVERY OF OH-NO$_2$-PYRENE ISOMERS IN FRACTIONATION STEPS

	Percent Recovery	
	3-HNP	6/8-HNP
A. Separately Performed Steps-Reagent Spikes Fractions Analyzed		
Acid/Base Partitioning(a,b)		
Acid Fraction	102	86
Neutral Fraction	0.2	0.2
Total Recovery	102	86
Silica Gel Column Chromatography(a,c)		
Hexane:Benzene	ND(d)	ND
Methylene Chloride	12	53
Methanol	7	5
Total Recovery	19	58
Silica Gel HPLC (Methanol:Methylene Chloride in Hexane Gradient)(a,e)		
Retention Window 31-39 min	73	78
Silica Gel HPLC (Hexane and Methylene Chloride Gradient)(f)		
Retention Window 9-25 min	25	52
B. Combined Steps		
Acid/Base Partitioning and Silica Gel HPLC		
Reagent Spike - Retention Window 31-39 min(g)	77	71
Matrix Spike - Retention Window 31-39 min(h)	60	45

(a) Duplicate analyses.

(b) Spike solution diluted to 50 mL with MeCl$_2$; partitioned 3 times with 40 mL of NaOH and H$_2$SO$_4$; aqueous phase back extracted 3 times with 40 mL MeCl$_2$; 3-HNP analyses ±10%; 6/8-HNP analyses ±10%.

(c) Spike solution solvent exchanged with hexane and placed at head of 10 g silica gel column; column eluted with 80 mL hexane and 140 mL each of hexane:benzene, methylene chloride and methanol; 2 mL of each elution solvent, used to rinse reagent spike vessel, was used as initial portion of eluent; 3-HNP analyses ±5%; 6/8-HNP analyses ±10%.

(d) None detected.

(e) Reagent spike concentrated to 100 μL; multiple analyses by HPLC method with pooled collection of retention window listed; analyses ±5%.

(f) Recovery estimated as ratio of HPLC UV response for triplicate analyses of standards using each HPLC gradient multiplied by recovery of preceeding step.

(g) Acid/base partitioning performed as in footnote (b) and acid fraction separated by HPLC as in footnote (e).

(h) Spike solution added to 50 mg of methylene chloride extract of NBS Standard Reference Material 1649 (Washington, D.C. Urban Air Particulate Matter); sample separated as in footnote (g).

TABLE III. RELATIVE RETENTION VALUES FOR SELECTED NO_2-FLUORANTHENE/NO_2-PYRENE ISOMERS AND OH-NO_2-FLUORANTHENE/OH-NO_2-PYRENE ISOMERS

Compound	Retention Relative to D9-1NP
Tentatively identified OH-NO_2-fluoranthene	0.865
1-NO_2-fluoranthene	0.944
7-NO_2-fluoranthene	0.951
2-NO_2-fluoranthene	0.966
3-NO_2-fluoranthene	0.971
2-OH-1-NO_2-fluoranthene	0.991
8-NO_2-fluoranthene	0.998
1-NO_2-pyrene	1.002
3-OH-2-NO_2-fluoranthene(a)	1.008
2-OH-1-NO_2-pyrene	1.041
10-OH-1-NO_2-pyrene	1.112
9-OH-1-NO_2-pyrene	1.203
4-OH-1-NO_2-pyrene	1.203
3-OH-1-NO_2-pyrene	1.217
6-OH-1-NO_2-pyrene	1.232
8-OH-1-NO_2-pyrene	1.232
5-OH-1-NO_2-pyrene	1.232

(a) Major product formed from direct nitration of 3-OH-fluoranthene and NaOH fusion of 2-NO_2-fluoranthene - private communication, L. M. Ball.

TABLE IV. RETENTION VALUES AND EI MS ION INTENSITIES OF OTHER TENTATIVELY IDENTIFIED OH-NO_2-PAH IN ACID-C FRACTION

Tentative Identification	Retention Relative to D9-NP	Mass (Percent Relative Intensity)							
		M	M-O	M-OH	M-NO	M-NO_2	M-CNO_2	M-OH-NO_2	M-CONO_2
OH-NO_2-benzene	0.395	139(100)	123(19)	ND[(a)]	109(36)	93(23)	81(20)	--[(b)]	--
OH-NO_2-methyl benzene	0.425 0.438	153(41) 153(100)	137(11) 137(15)	136(100) ND	123(4) 123(29)	107(10) 107(14)	95(10) 95(6)	90(21) 90(<1)	-- --
OH-NO_2-C_2 alkyl benzene	0.460 0.469 0.483	167(100) 167(80) 167(100)	151(16) 151(14) 151(18)	ND 150(100) 150(50)	137(25) 137(3) 137(16)	121(13) 121(10) 121(14)	109(5) ND 109(3)	104(2) 104(8) 104(14)	93(10) 93(8) 93(6)
OH-NO_2-naphthalene	0.705	189(100)	173(14)	172(5)	159(23)	143(26)	131(23)	126(9)	115(89)
OH-NO_2-methyl naphthalene	0.693	203(100)	187(8)	186(24)	173(27)	157(20)	145(14)	ND	129(31)
OH-NO_2-acenaphthene	0.685	215(100)	199(8)	198(1)	185(14)	169(5)	157(9)	152(3)	141(36)
OH-NO_2-methyl acenaphthene	0.810 0.921	229(100) 229(100)	213(7) 213(24)	212(ND) 212(ND)	199(40) 199(36)	183(24) 183(18)	171(14) 171(15)	166(5) 166(ND)	155(35) 155(56)

(a) Not Detected.

(b) Instrument not scanned low enough to detect this ion.

TABLE V. CONCENTRATION OF OH-NO_2-PAH AND NO_2-PAHs IN AMBIENT AIR PARTICULATE SAMPLE

Component	Concentration in Component Material		
	OH-NO_2-Fluoranthene	2-NO_2-Fluoranthene[a]	1-NO_2-Pyrene
Organic Acid Fraction	70 µg/g	NA[b]	NA
Hexane:Benzene Fraction	NA	50 µg/g	0 µg/g
Methylene Chloride Fraction	0.1 µg/g	NA	NA
Particulate Extract[c]	4.8 µg/g	6.4 µg/g	2.6 µg/g
Stage III Particles[d]	0.19 µg/g	0.25 µg/g	0.10 µg/g
Ambient Air[e]	0.008 ng/g	0.01 ng/m^3	0.004 ng/m^3

(a) Recent analyses with reference 2-NF and 3-NF have shown that 2-NF incorrectly identified as 3-NF in Wise, et al. (27).

(b) Not applicable.

(c) CH_2Cl_2 extract of MAVS Stage III particles.

(d) MAVS Stage III particles, <1.7 µm.

(e) Respirable particles, <1.7 µm.

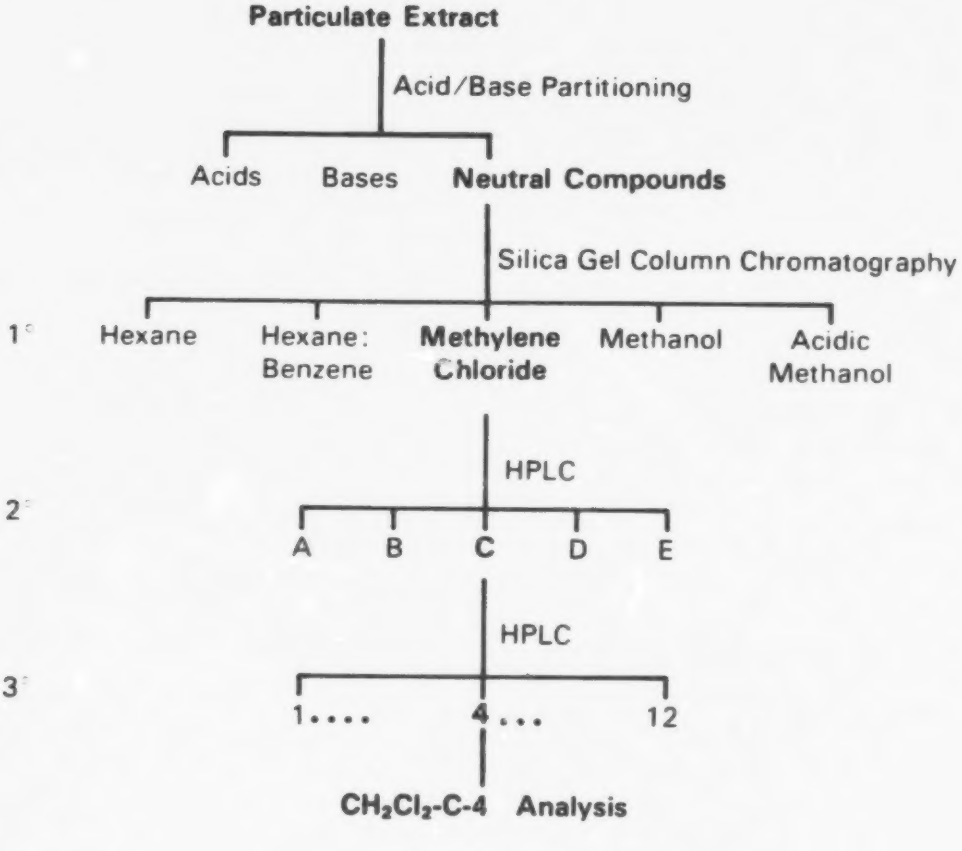
Particulate Extract
Acid/Base Partitioning
Acids
Bases
Neutral Compounds
Silica Gel Column Chromatography
1°
Hexane
Hexane: Benzene
Methylene Chloride
Methanol
Acidic Methanol
HPLC
2°
A
B
C
D
E
HPLC
3°
1....
4...
12
CH_2Cl_2-C-4 Analysis

FIGURE 1. OVERVIEW OF FRACTIONATION SCHEME. BOLD FACE TYPE INDICATES PATHWAY LEADING TO ANALYSIS OF MUTAGENIC SUBFRACTION CH_2Cl_2-C-4.

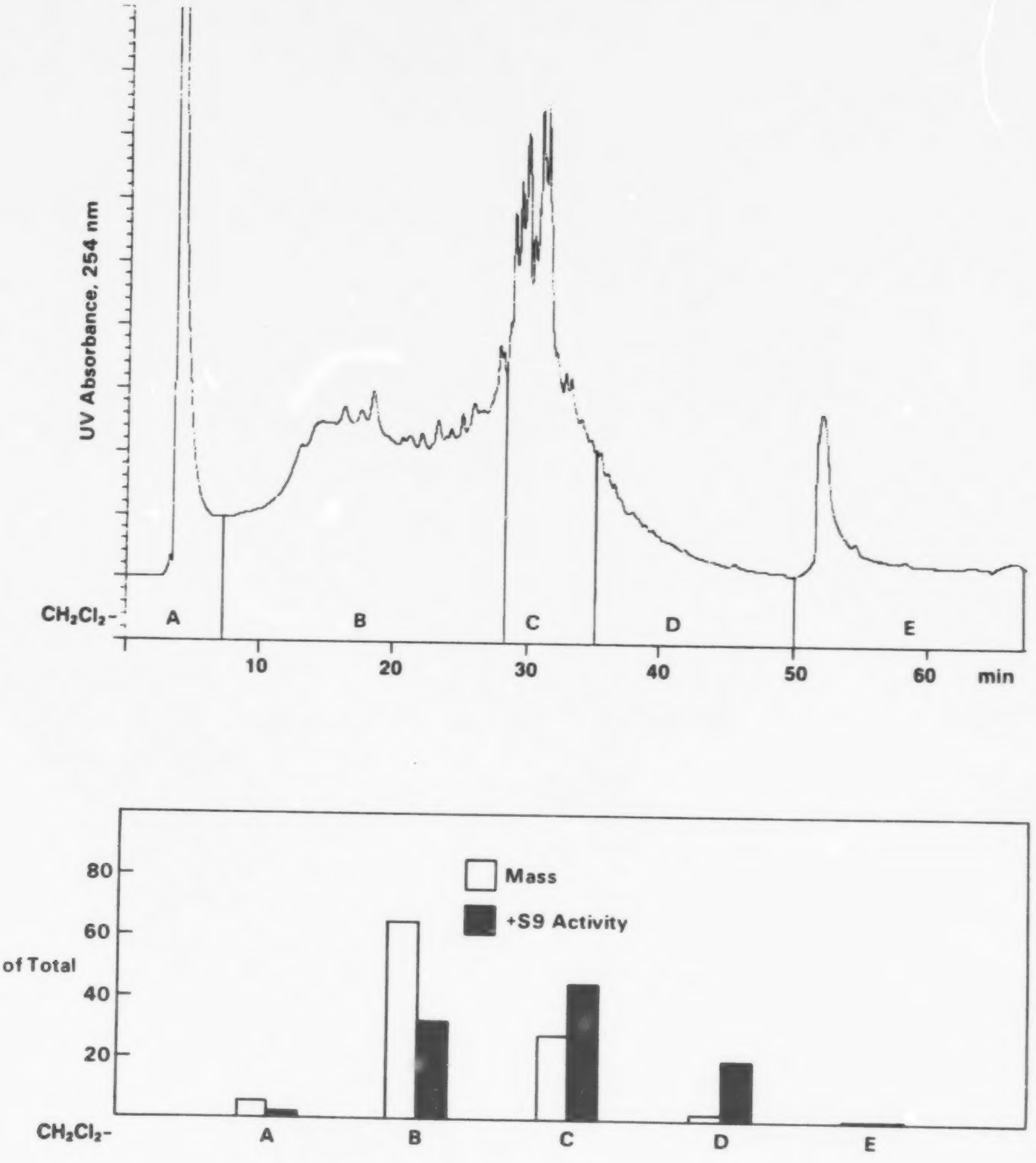

FIGURE 2. UV CHROMATOGRAM FOR HPLC SEPARATION OF CH_2Cl_2 FRACTION. PERCENTAGE DISTRIBUTION OF RECOVERED MASS AND ACTIVITY (TA 98, +S9) OF FIVE SUBFRACTIONS INCLUDED.

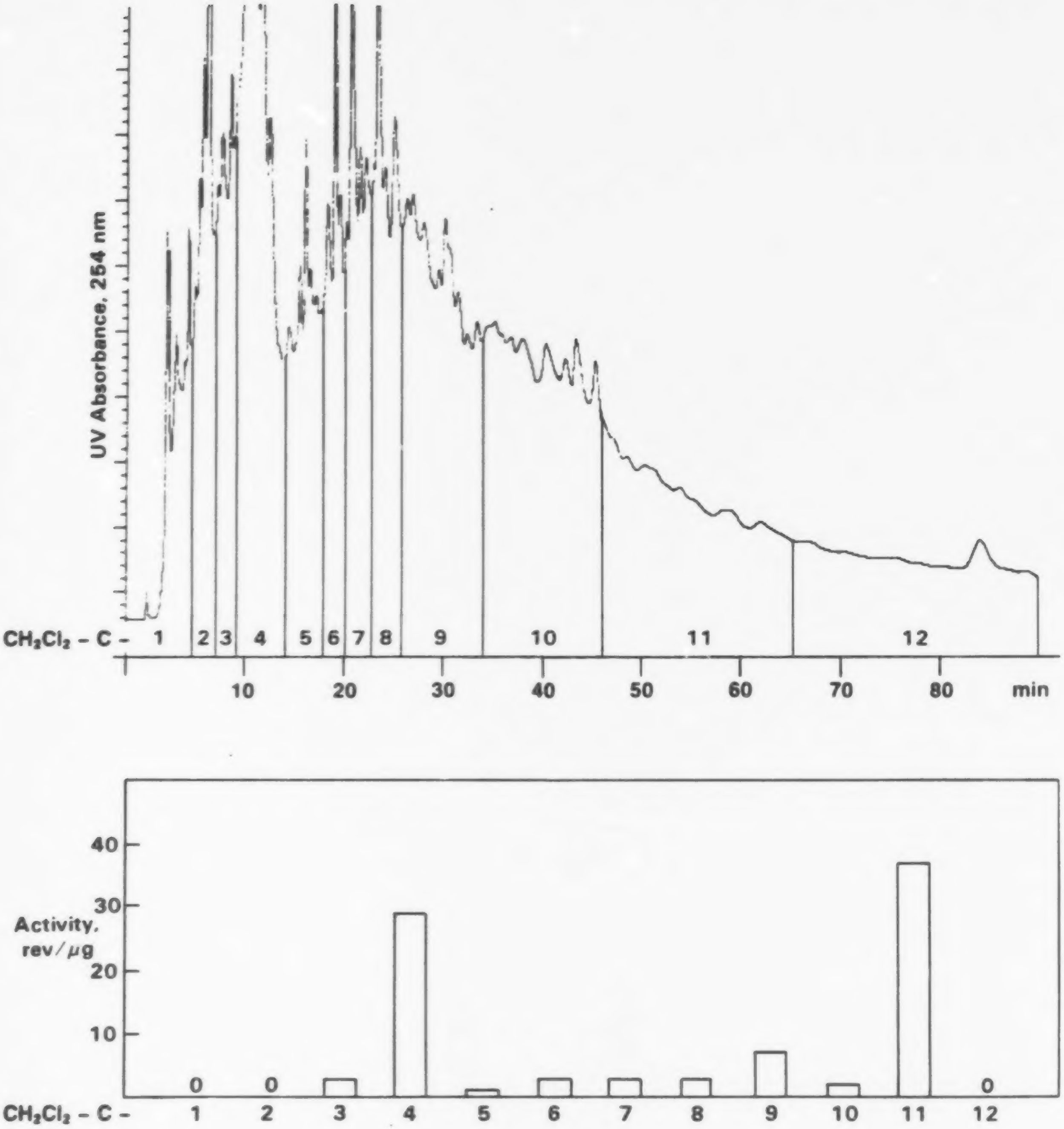

FIGURE 3. UV CHROMATOGRAM FOR HPLC SEPARATION OF CH_2Cl_2-C FRACTION. MUTAGENIC ACTIVITY (TA 98, +S9) OF TWELVE SUBFRACTIONS INCLUDED.

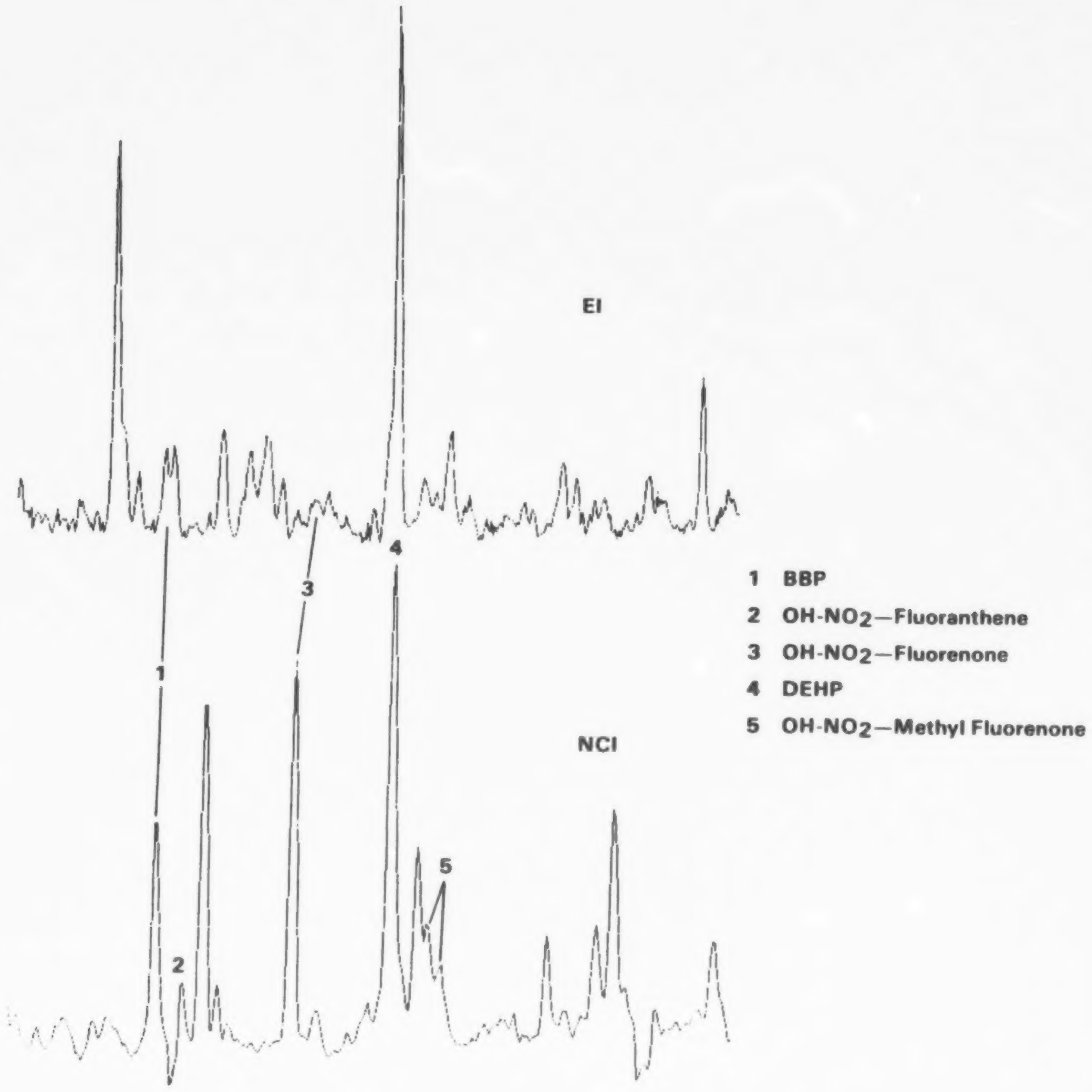

FIGURE 4. SELECTED RETENTION WINDOWS FROM EI AND NCI HRGC/MS ANALYSES OF CH_2Cl_2-C-4. BBP (BUTYLBENZYLPHTHALATE) AND DEHP (DI-2-ETHYLHEXYLPHTHALATE) USED TO ALIGN THE TWO CHROMATOGRAMS.

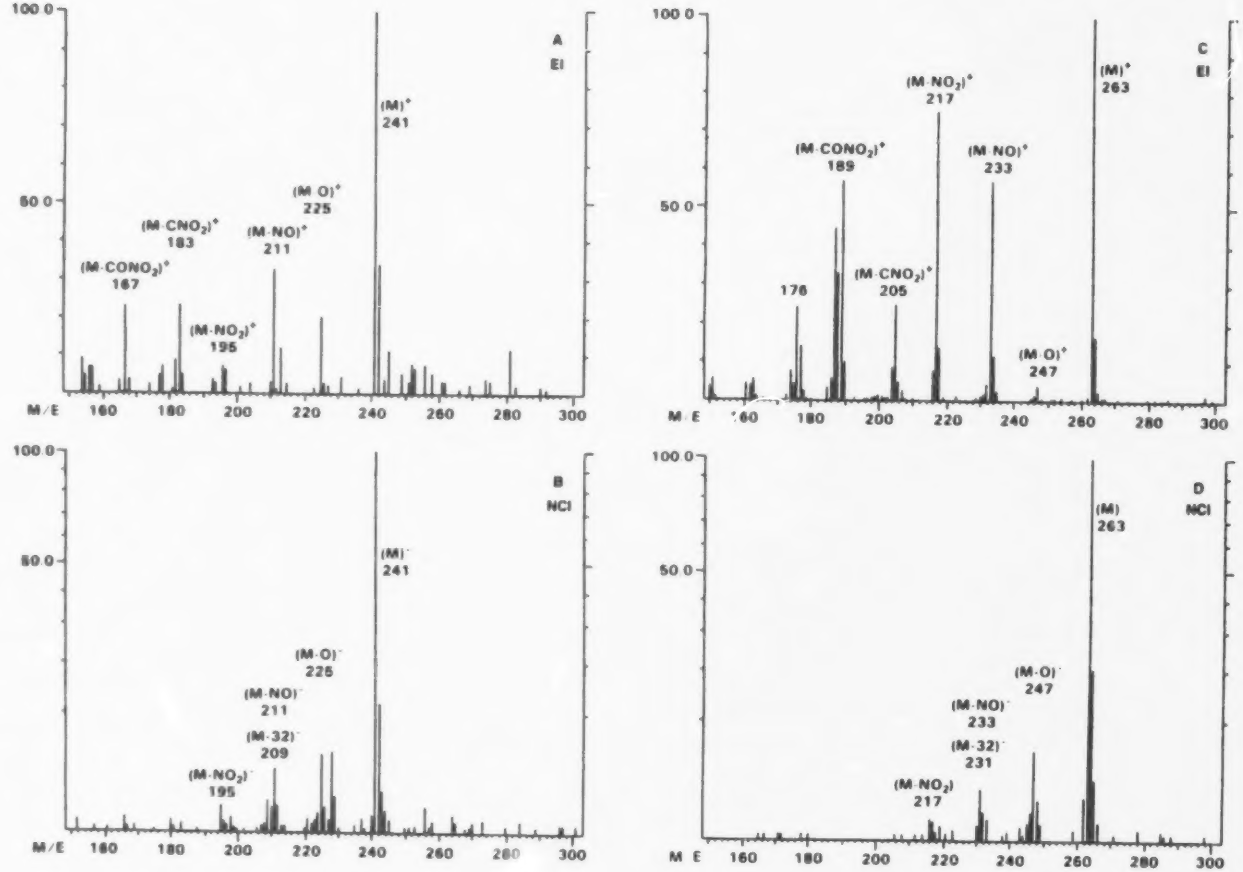

FIGURE 5. MASS SPECTRA OF OH-NO_2-PAHs. OH-NO_2-FLUORENONE IN CH_2Cl_2-C-4: A - EI SPECTRUM, B - NCI SPECTRUM. REFERENCE COMPOUND 6-OH-1-NO_2-PYRENE: C - EI SPECTRUM, D - NCI SPECTRUM. EI SPECTRA - LINEAR INTENSITY SCALE. NCI SPECTRA - SQUARE ROOT INTENSITY SCALE USED TO EXPAND THE DISPLAY OF LOW INTENSITY FRAGMENT IONS.

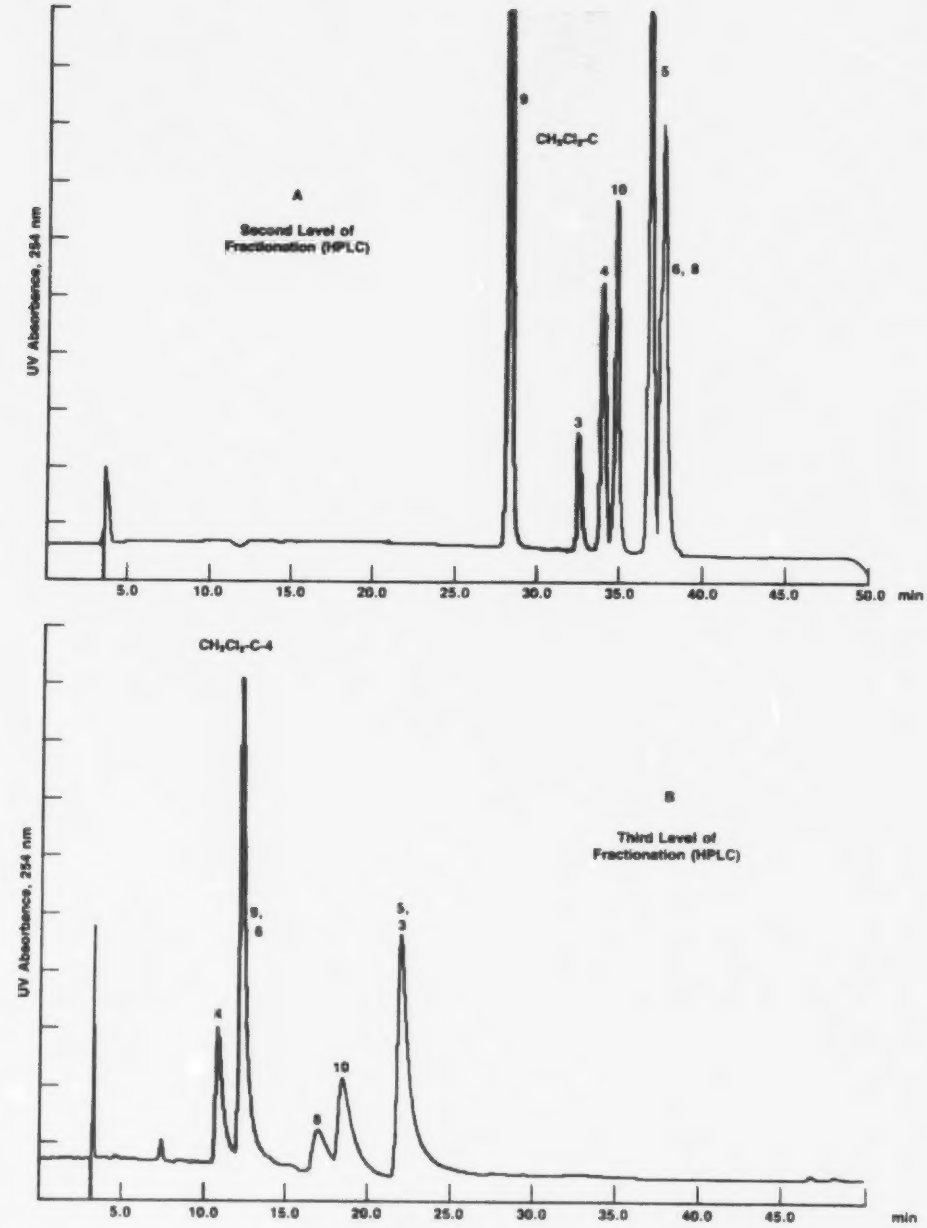

FIGURE 6. HPLC UV CHROMATOGRAMS OF HNP ISOMERS. A - HPLC GRADIENT OF METHANOL/METHYLENE CHLORIDE (2:98, v:v) IN HEXANE, USED AS SECOND LEVEL OF FRACTIONATION FOR SEPARATION OF PARTICULATE EXTRACT FRACTION CH_2Cl_2. SHADED REGION CORRESPONDS TO RETENTION VOLUME OF CH_2Cl_2-C. B - HPLC GRADIENT OF METHYLENE CHLORIDE IN HEXANE, USED AS THIRD LEVEL OF FRACTIONATION FOR SEPARATION OF PARTICULATE EXTRACT FRACTION CH_2Cl_2-C. SHADED REGION CORRESPONDS TO RETENTION VOLUME OF CH_2Cl_2-C-4. NUMERALS IN FIGURE INDICATE THE OH SUBSTITUENT POSITION OF OH-1-NO_2-PYRENE ISOMERS ANALYZED.

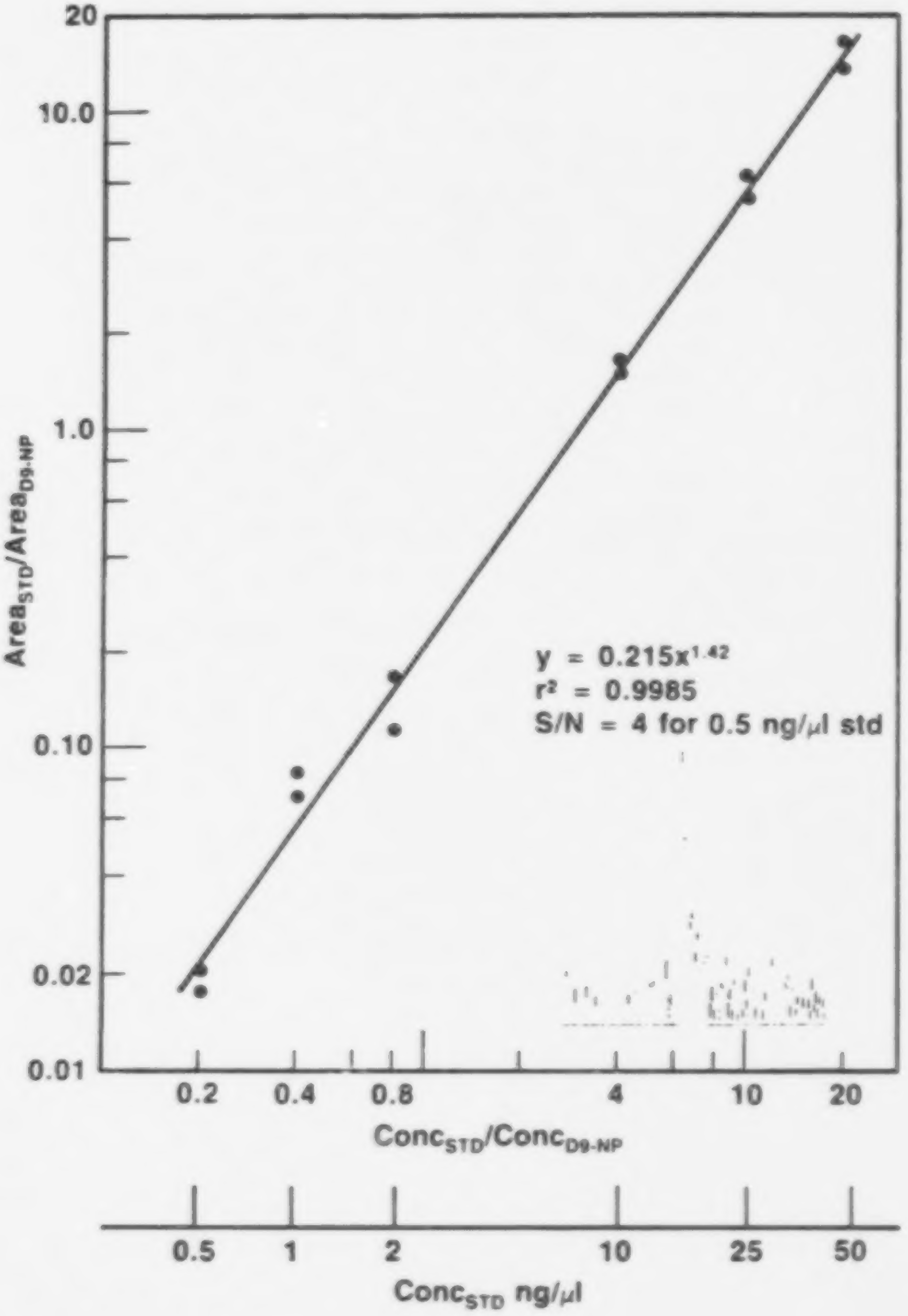

FIGURE 7. REPRESENTATIVE CALIBRATION CURVE FOR NCI HRGC/MS QUANTIFICATION OF 6/8-HNP.

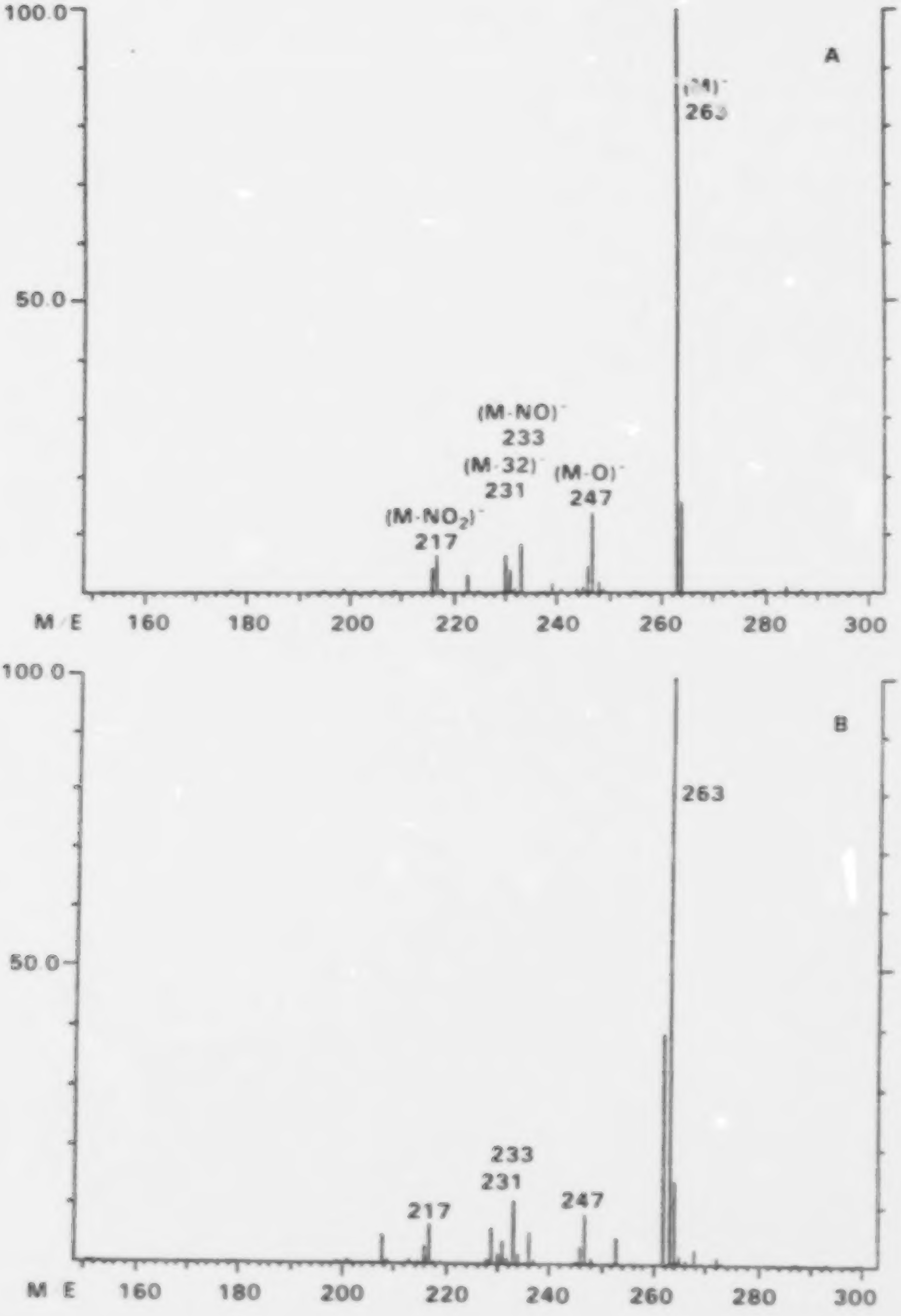

FIGURE 8. NCI MASS SPECTRA OF OH-NO_2-FLUORANTHENE ISOMER IN AMBIENT AIR PARTICULATE EXTRACT. A - SPECTRUM OF COMPOUND IN CH_2Cl_2-C-4 FRACTION. B - SPECTRUM OF COMPOUND IN ACID - C FRACTION.

SOLID SAMPLE INTRODUCTION INTO THE INDUCTIVELY COUPLED PLASMA.

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SOLID SAMPLE INTRODUCTION INTO THE INDUCTIVELY COUPLED PLASMA.

1. LIQUID SAMPLE ANALYSIS

1.1 ATOMIC EMISSION WITH THE INDUCTIVELY COUPLED PLASMA

1.1.1 ABSTRACT:

A wire loop was used with the direct sample insertion device (DSID) for atomic emission spectrometry with the inductively coupled plasma (ICP). Detection limits are improved by approximately a factor of 10 to 100. Spectral overlaps can in some cases be eliminated by the temporal resolution provided by the wire loop system. Certain matrix effects which disturb conventional sample introduction systems are eliminated or minimized by this system.

1.1.2. MAIN BODY.

Before embarking on the direct analysis of solid samples using the Direct Sample Insertion Device (DSID) for the Inductively Coupled Plasma (ICP) it was deemed useful to gain knowledge of the behavior of the DSID with desolvated liquid samples. In attempting to determine the physical temperature of a graphite electrode placed in the plasma by the melting points of metals, it was found that tungsten wire could be inserted into the plasma with no effect other than the embrittlement of the wire. A new direct sample insertion device was designed and constructed to permit rapid placement of a tungsten wire loop into the plasma. This device was pneumatically driven to provide near instantaneous entry of the wire into the plasma as was found necessary by the short vaporization times of the sample elements. This system has since been replaced with a more versatile stepper motor driven system which will be discussed in section 1.3.

Liquid samples (10ul) placed on the wire are desolvated by placing them at roughly 20 to 30 mm below the top of the load coil with the plasma ignited. The heat of the plasma and the flow of gases around the wire ensured rapid (10 to 30 s) drying of the sample on the wire. This drying step is easily monitored since three phenomena are observed during this time: 1) the plasma constricts itself due to the presence of di- and poly- atomic molecules 2) the reflected power increases slightly 3) the signal intensity rises as the plasma is constricted into the viewing zone. Once dry, the wire is inserted into the plasma with the transient emission signal occurring 50 to 400 ms after insertion and having a half width of approximately 100 ms. Under fixed conditions, the standard deviation on the time occurrence of the analyte peak emission is about 3 ms. The extremely high precision of this occurrence may allow spectrally overlapping lines to be resolved in the time domain. We have observed temporal resolution in at least one case.

With the wire loop direct sample insertion device, the detection limits listed in Table I have been obtained. Table I compares the detection limits obtained with the wire loop DSID to those obtained by Winge et al. (*Appl. Spectrosc.*, 1979, 206-219) using nebulization and which are often used as a comparative measure. The wire loop DSID is providing detection limit improvements of a factor of 10 to 100. The relative standard deviation of the signal well above the detection limit is occasionally as good as 1% but is typically 5 to 10% for manual sample delivery. An automated sample deposition device has been developed to operate with the stepper motor driven DSID described in section 1.3. With the automated sample deposition, the relative standard deviation is consistently 1 to 2 % over periods as long as 3 hours.

Table I. Wire Loop DSID Detection Limits.

Element	Wavelength	Detection Limit		
	nm	Conc. ng/ml	Absolute pg	Fassel ng/ml
Copper	324.754	0.2	2	5.4
Zinc (a)	213.856	0.07	0.7	1.8
Cadmium (a)	228.802	0.3	3	2.7
Silver	328.068	0.04	0.4	7
Lead (a)	220.351	3	30	42
Magnesium	280.269	0.007	0.07	0.30

(a) Tantalum wire required due to insufficient temporal resolution from Tungsten spectral overlap.

Difficulties have arisen in the use of Tungsten as a sample support. A certain amount of Tungsten oxidizes during the drying of the liquid sample and, because of the large number of Tungsten lines, spectral overlaps are common. The temporal resolution of the overlaps is not sufficient in many cases (Pb,Cd,Zn) and in others, the processing of the data is rendered more difficult. Experiments with Tantalum show that it would be preferable to Tungsten in many aspects. Tantalum has fewer lines than Tungsten and is less reactive and so should and does provides fewer spectral interferences. Equally important, Tantalum oxide is the least volatile of the oxides consequently ensuring adequate temporal resolution of spectral overlaps. Unfortunately, the lifetime of tantalum sample supports is significantly shorter than that of tungsten sample supports. This requires frequent replacement of the tantalum sample supports. Experiments have shown that, given the present method of manufacturing the sample supports and mounting them on the DSID, the change in signal resulting from the replacement of sample supports is of the order of 5%. It is expected that improved sample support manufacturing and mounting can possibly eliminate any change in response.

The weight, more specifically the total heat capacity, of the sample support has been found to contribute significantly to the performance of the DSID technique which exhibits DC arc type response. With a tungsten wire of twice the mass, the peak occurred approximately 1. 5 times later and had a half width 1.5 times longer. The S/N level was one half that of the thinner wire. The geometric configuration of the support also plays an important role, it appears that the larger the exposed area, the more rapid the heating and evolution of the analyte. The different elements volatilize at different times, the order of which is quite similar to that found in DC arc spectrometry. This differential volatilization is beneficial in that spectral overlaps are temporally resolved in many cases.

In the presence of high salt concentrations (1000 ppm Ca) the peak heights and shapes are altered but the peak areas remain essentially the same as for the pure aqueous standards. This indicates a relative freedom from matrix effects, since the total emission signal is directly related to the concentration. Our later work with inductively coupled plasma (ICP) mass spectrometry (MS) confirms these findings. This will be discussed in section 1.2.

1.2 WIRE LOOP DIRECT SAMPLE INSERTION FOR ICP SOURCE MASS SPECTROMETRY

1.2.1 ABSTRACT.

The wire loop technique was used to introduce aqueous samples into the ICP for mass spectrometry. A new device was constructed and installed at the Rexdale MOE facility. Mass Spectrometry detection limits were improved by a factor of approximately 40. Matrix and wire effects seem to be minimal. Sample throughput may be substantially improved with this system. A Tungsten (rather than Tantalum) wire loop is necessary.

1.2.2. MAIN BODY.

We speculated that the wire loop-DSID technique would provide the same advantages for ICP-MS that it does for ICP-AES for liquid samples. Probably solid samples can still be run more appropriately with an ICP-AES system due to the possibility of clogging the mass spectrometer. It is quite conceivable that the two spectroscopic methods can be combined for certain applications.

In conjunction with Mr. David Boomer of the Inorganic Trace Contaminants Section we designed, built and installed a DSID device for use on their new SCIEX Elan 250 ICP-MS. It was felt by Mr. Boomer and myself that this was an important and logical path for the research to take while we were actively working with the wire loop DSID system. The initial results are very promising. Even with the first generation of software, which is not designed for transient signals, we were able to achieve an order of magnitude improvement in the detection limits. Precision was approximately 6% RSD. As we stated in the previous section, this can certainly be improved upon with an automatic sampling-injection system.

No matrix or mass spectral overlap problems were encountered with the W wire. Ta is unsuitable for horizontal operation since the temperature is just sufficient to allow the wire to soften and bend. Since the liquid sample is dried prior to insertion, the analyte enters the plasma without the water vapor which normally accompanies it with conventional sample introduction by nebulization. This leads to an unexpected benefit. By eliminating the water from the plasma during the sample vaporization, the formation of the oxides of the elements is severely reduced. These oxides are the source of significant mass spectral overlaps in conventional ICP-MS (e.g. ArO on Fe). This is especially important with the molecular O^2 overlap with S^{32}. Sulfur is an important element which can be difficult to determine at low levels by optical methods. The elimination of water also means that more energy appears to be available for ionization and sample breakdown. The temporal resolution may prove advantageous in cases where isotopes overlap.

1.3. WIRE LOOP STEPPER MOTOR DRIVEN DIRECT INSERTION DEVICE.

1.3.1. ABSTRACT.

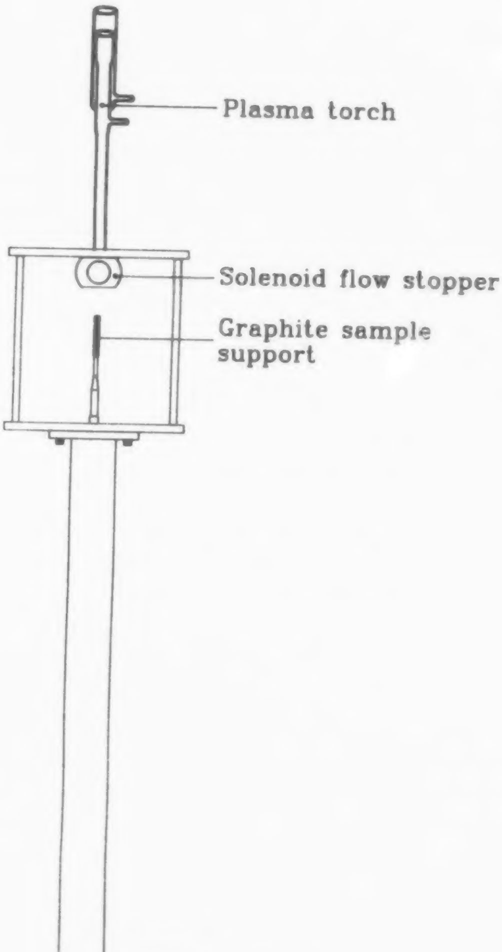
A stepper motor driven DSID was developed. The system provides RS-232 serial control and can be used with or without supporting computer. Sufficient speed is provided for wire loop insertion. The flexibility allows the system to be used for solid sample ashing, drying and insertion.

1.3.2 MAIN BODY

The pneumatic DSID performed well for desolvated liquid samples applied to the wire loop sample support. It did, however, suffer from two major deficiencies for solid sample analysis: the ejection of the sample by the sudden insertion into the plasma and the lack of fine control of the movement. Drying and ashing steps might be necessary for solid samples and, since the heating is achieved by moving the sample support closer to the plasma, fine control of the velocity and position is required. A stepper motor design of the DSID was developed (Figure 1) to provide the additional control necessary for the solid samples while still providing the speed required for the wire loop DSID work. The direct drive configuration of the stepper motor DSID design using a 1 inch sprocket provides linear velocity up to 15 inches/second. This velocity was demonstrated by experiment to be sufficient for the wire loop DSID work.

The fine control of the position of the sample support enabled the cooling of the sample support in the lower section of the plasma torch, thus eliminating the need for a sealed sample chamber as was required with the pneumatic DSID. A computer controlled solenoid driven port now ensures the sealing of the base of the torch while the sample support is retracted. The 'wide open' sample area makes the sample support very accessible for manual or automated sample application. A simple automatic liquid sample deposition device was developed for use with the wire loop DSID and provides significantly improved reproducibility and sample throughput. A versatile robotic (or micro-robotic) manipulator for the mounting of sample supports containing solid samples is presently being designed.

FIGURE 1



2. SOLID SAMPLE ANALYSIS

2.1 ANALYSIS OF HAIR.

2.1.1. ABSTRACT:

The DSID was demonstrated to be capable of the direct analysis of single strands of hair without ashing or other sample preparation. The precision is element dependent. The accuracy is within 40% and may be better.

2.2.2. MAIN BODY.

A number of hair samples were analyzed by a variety of accepted procedures. The results were in good agreement. We now have three standardized hair samples and well developed procedures for new samples.

Our initial work with conventional electrodes was unsatisfactory. A new electrode with a deep well was developed. This allowed the insertion of one or several strands directly into the plasma without any ashing or drying step. Our calibration was carried out using water samples. This is essentially ideal due to the simplicity of water standard preparation (or commercial availability). The peak areas and time behavior of a given element in a hair sample appear to be identical with that in an aqueous sample. This drastically simplifies analysis procedures and requires only a simple standard preparation step.

The precision of the technique was element dependent. Copper had a relative standard deviation (RSD) of 30 % while Zn had an RSD of 10 %. The literature demonstrates that this is to be expected as Cu concentration is often dependent on the ldistance from the scalp, while Zn is relatively independent. The Cu precision can probably be improved by the insertion of multiple strands in a given insertion. The Zn RSD is typical of the DSID device and can only be improved by multiple insertions.

The accuracy varies from sample to sample. It appears that we had trouble with certain elements with one donor, but other elements with another donor. With the low number of donors it was impossible to make more emphatic statements. In no case was the error worse than 40%. If an average correction value is used, since all values were high, the maximum error drops to 20%. This will be acceptable for some work, e.g. toxicology, but may not be adequate for others. Certainly this is a marvelous rapid survey technique as it stands. More work needs to be done to clarify the accuracy problem.

2.3. SEDIMENTS.

2.3.1. ABSTRACT:

Solid sample studies of estuarine sediments have been initiated recently. Detection limits appear to be adequate for the qualitative identification of toxic elements, but the accuracy and precision is not adequate yet for quantitative work. Various instrumental problems are discussed.

2.3.2. MAIN BODY:

The sediment types recommend by Mr. Boomer of the MOE were acquired. These include BCSS-1, MESS-1 and SRM 1646 . We initiated our work with these after the stepper motor DSID (section 1.3) was completed. After initially profiling the samples for detection limits for the toxic elements (see Table II),we began work on stabilizing the signal level for Cu. Copper is an element which we commonly study and is in relatively high concentration in all these samples. Once we have stabilized with Cu, then we expect that we will have improved our precision and accuracy for all the elements. Our precision at this stage (two months of work) is still at such a level that we can not make substantial statements about the need for special standards. Our hope is that graphite based standards, containing oxides of the analyte, will work, however the time behavior is drastically different between each of the sediments and the graphite standards. We also believe at this time that a certain amount of our precision problems arises due to inhomogeneity problems. Since we only use 1 to 10 mg per insertion, this is quite possible. Our own "home made" standards which are more finely ground (about the same mesh as the sediments)have provided higher precision.

Table II. Detection limits in solid sediments estimated for MESS-1.

Element	Certified concentration μg/g	Estimated detection limit based on 2 mg sample μg/g
Cu	25.1	0.8
Cd	0.59	0.2
Zn	191	8
Pb	34.0	2
Mn	513	32

We believe that it may also be necessary to use either mixed gases or fluxing agents when preparing the samples. In the matter of sample preparation we believe that the processes can be conveniently and very effectively automated using a commercially available robot. This could be quite cost effective since the same robot can be used for dc arc and other sample preparation procedures as well as incorporated into the DSID process.

Rapid background correction is required for samples which generate a large amount of stray light, and this is discussed in the next section.

3. DETECTION SYSTEM REQUIREMENTS FOR DSID OPERATION

(REFRACTOR PLATE BACKGROUND CORRECTION)

There are two methods of background correction presently available on commercial direct reading spectrometers. These are vibrating slits and refractor plates. Vibrating (moving) slits are limited to relatively slow movement and actually view a slightly different portion of the plasma when spectrum shifting. This is not a problem with conventional sample introduction system, because the sample is uniformly distributed though a large central aerosol channel in the plasma, however this is not satisfactory with the DSID system.

Refractor plates shift the entire spectrum after it has been imaged onto the entrance slit and consequently are adequate for this type of work. In the Thermo Jarrell-Ash line of spectrometers these are mounted on galvanic drives and consequently are capable of rapid movement, though the normal software does not provide this capability. On the system that we are acquiring, we will be working with Thermo Jarrell-Ash to develop software and hardware suitable for the high speed acquisition of spectrally background corrected signals.

ELECTROTHERMAL VAPOURIZATION FOR SAMPLE INTRODUCTION INTO A PLASMA FOR PLASMA SOURCE MASS SPECTROMETRY

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and

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1.0 INTRODUCTION

Inductively coupled plasma source mass spectrometry (ICP/MS) is still in its infancy as a method of chemical analysis. A 1985 comprehensive review of ICP/MS by Douglas and Houk [1] lists 54 references. Since this report has been written there have been between 20 and 30 other reports published in this field. The rapidly rising rate of appearance of publications mirrors the commercial introduction of ICP/MS equipment three years ago.

Most workers in this field use conventional nebulization (concentric and cross flow) systems for sample introduction into the ICP. Using this approach detection limits up to 2.5 orders of magnitude better than flame atomic absorption spectrometry (AAS) and plasma optical emission techniques have been reported. These powers of detection approach or, in some cases, equal furnace AAS. Despite these excellent powers of detection, for many investigations (e.g., environmental, biological and clinical), it would still be a distinct advantage to achieve lower values.

The direct injection of $\mu\ell$ aliquots of sample into the plasma in plasma optical emission spectrometry has yielded at least 1 order of magnitude better detection limits compared to conventional nebulization. Such an approach has the advantage over conventional nebulization that small samples (volume limited), highly viscous samples and possibly solid samples can be run. There are a variety of ways this can be done [2]. These include (1) direct insertion of sample along the sample uptake channel using wires or graphite rod, (2) micro-arcs or sparks within or outside of the torch system, and (3) electrothermal vapourizers (ETV). We have chosen to investigate the utility of number 3.

"Potential" advantages over the other two direct insertion methods include:

(1) Use of a larger sample size.

(2) Opportunity for matrix modification.

(3) Closely controlled, multiple heating cycles.

Early results with an Re filament and a graphite filament ETV are reported below.

Another, related, investigation was also undertaken. Mass spectrometry has been a very useful and important detector for gas chromatography since 1957 [3]. In this application the MS and GC are interfaced so that the atmospheric pressure GC effluent is transferred through a region with a large pressure drop until the desired constituent enters the MS at a pressure of less than 10^{-6} torr. The introduced effluent is also subjected to an appropriate method of ionization prior to mass separation and detection. The inductively coupled plasma could be used as an excellent ion source for this application. In this way the mass spectrometer becomes an element specific detector for chromatography. There is an urgent need for environmental, toxic metal-organic compound data and the ICP source mass spectrometer should be an excellent detector for chromatography in this application. This detector is isotope specific and thus would, in comparison with other important, but only, element specific detectors (AAS, AES, AFS), be capable of producing important additional information on the occurrence of toxic metal organic species in the environment. In the following, the first recorded (preliminary) data is given, outlining the use of ICP source mass spectrometry as an element specific detector for gas chromatography.

2.0 EXPERIMENTAL

2.1 Equipment

The ICP/MS apparatus used was designed by Douglas and French [4] at the Institute for Aerospace Studies, University of Toronto. Further development by Sciex, Thornhill, Ontario, Canada, has resulted in a commercial product, the ELAN.

The electrothermal vapourizer (ETV) was developed for the purposes of this investigation and its design and optimum operation are described in detail previously [5]. A summary of its characteristics are in Table 1. The filament consists of 0.05 mm thick Re metal ribbon (available from REMBAR Laboratory, New York) of sample capacity 5 µℓ, which can be resistively heated using a crude home-made power supply. This is constructed from a 1 KW transformer and lab variac. Maximum output capability is 2.5V and 30A. The filament is encased in a glass dome which is sealed to a metallic base by an "O" ring. Argon is flowed through the device to carry the vapourized sample, via the Tygon tubing, into the ICP.

Table 1. Summary of ETV Characteristics

Volume of glass dome above filament	5 mℓ
Inert gas introduction	Tangential at base (~4 ℓ/min) laminar flow (Reynolds number of system is 150)
Filament	Re metal (central sample dimple 1 mm deep by 5 mm diameter - 5 µℓ capacity)
Maximum temperature	1900°C (above this severe plasma loading occurs due to Re loss)
Particle size of aerosol	0.5 to 1.0 µm (Zn)
Transport efficiency* at 4ℓ/min (%)	Cd(85), Pb(83), Cu(84), Fe(85), Ni(83)

*Greatly improved compared to previously listed devices [2].

The ICP was obtained from Henry Radio (Model 2500). Output powers of up to 2 KW are achievable. This device must be operated and adjusted for the most part manually. A standard cross-flow nebulizer for solution sample introduction, when required, was used for initial optimization of ion optic and MS parameters for each element.

Mass selection is achieved with a quadrupole mass spectrometer. The quadrupole is particularly well suited for mass analysis using a plasma source. The 10^{-4} to 10^{-5} torr operating pressures tolerated by quadrupoles reduce the pumping speed requirement and allow the use of relatively large orifices. Fringing field effects which are encountered at the entrance and exit of quadrupoles are minimized by the use of short sections of AC only quadrupole rod sets. This provides improved resolution capability.

The interface of the plasma to the ion optical system consists of a sample orifice approximately 0.4 mm in diameter. The orifice is a nickel conical structure mounted on a water cooled copper flange. Immediately behind the sample and separated by a region (12 × the diameter of the orifice) which is pumped mechanically to about 1 torr, is a skimmer orifice 1 mm in diameter.

A cryogenic pumping system, supplied by CTI-Cryogenics Ltd., is capable of pumping the mass spectrometer down to a pressure of about 2×10^{-5} torr during operation.

A Model 9176 x-y recorder, available from Varian, was employed for display of spectra. Operating conditions for the equipment are given in Table 2.

Table 2. Instruments and Operating Conditions

Operating Conditions:	
Forward power	1.25 KW
Reflected power	0 W (as close to this as possible)
Coolant flow	14 ℓ/min
Auxiliary flow	0.7 ℓ/min
Carrier flow	2 ℓ/min
Drying	100°C for 20 sec
Ashing	(400-800°C) - depends on type of sample and element
Vapourization	(up to 1800°C)
Clean-out	(2500°C)

A Fisher Scientific Series 2400 temperature programmable oven was used. The experimental parameters are given in Table 3.

Table 3. Gas Chromatographic Experimental Parameters

Column	3% OV-1 on Chromasorb W (80/100 mesh)
Gas flow rate	Argon at 8 mℓ/min oxygen (into transfer line) at 3 mℓ/min
Injector temperature	250°C
Temperature program	Isothermal 60°C to end of peak (1). Isothermal 250°C to end of chromatogram.
Transfer line (stainless - 0.5m length) temperature	Just high enough to ensure no breakup of peak ~200°C (using Variac and heating tape).
Interface	Transfer line connector (Swagelok) to base of ICP torch

2.2 Reagents

All metal salts, solvents and acids used were Reagent Grade quality or better. Atomic absorption standard solutions of metals 1 mg/mℓ in concentration, were obtained from Fisher Scientific.

Calibrating solutions (μg/mℓ) were prepared by dilution of the 1000 μg/mℓ standards. For preparation of μg/mℓ calibrating solutions the 10 or 1 μg/mℓ calibration solutions were diluted. All calibration solutions were single element and were made to contain 1% nitric acid upon final dilution. The concentration range covered was 1 μg/mℓ to 10 μg/mℓ.

National Bureau of Standards (Washington, D.C.) Standard Reference Samples were used to test the methodology. Samples analysed were Orchard Leaves (SRM 1571), Oyter Tissue (SRM 1566) and Pb Isotope Standards SRM 981 and SRM 983.

The following Sn compounds were prepared by pentylation using the method described by Maguire and Hunealt [6] - Me_3SnPe, Me_2SnPe_2 and $MeSnPe_3$ (PAe is methyl and Pe is pentyl).

2.3 Proposed Procedure for ETV Sample Introduction

(The system must be pumped down to 1 torr in the interface region and 2×10^{-6} torr in the mass spectrometer. This takes approximately 2.5 hours from a cold start.) Turn on all electronic systems and ignite the plasma. Aspirate a 1 μg/mℓ solution of the element to be determined. Optimize the ion optic components so that maximum analyte signal is obtained. The instrument must then be left operating until any analyte signal drift has stopped, a minimum of 1 hour. At this point the system is changed from nebulizer to ETV operation.

Orchard Leaves (SRM 1571) and Oyster Tissue (SRM 1566) samples are dissolved in closed Teflon digestion vessels by the method of Brzezinska et al [7]. A mixture of HNO_3, $HClO_4$ and HF is used. The acid content of the solutions after dilution to final volume is 1% in HNO_3.

Sample and standard solutions are analyzed as follows. Remove the glass dome from the ETV. Pipe a 2 μℓ aliquot of sample or standard solution onto the Re filament. (The auxiliary Ar flow, 2 ℓ/min, of argon to the plasma bypasses the ETV during this operation.) Replace the glass dome and clamp it tightly onto the ETV base using the toggle clamps. Divert the ETV Ar flow of 2 ℓ/min by means of the 3-way stop cock through to a fume hood vent. Dry the solution at about 100°C until the drop of liquid has been completely evaporated (visual observation). Char the standard or sample, if necessary at 400° to 800°C for 30-60s.

Using a 3-way stop cock switch the ETV Ar flow (at 2 ℓ/min) to pass into the plasma. Then turn off the auxiliary Ar flow. Vapourize the sample at up to 1800°C. Record the transient signal obtained. Signal integration must be used in computing elemental concentration in Orchard Leaves and Oyster Tissue solutions.

Calibration is done by the method of standard addition as follows. Run the sample alone, as outlined above. Then add 2 μℓ of suitable concentration of calibrating solution to the Re filament and dry as indicated above. Remove the glass envelope and add 2 μℓ of the sample solution and dry again as detailed above. Then vapourize the material on the Re filament according to the above procedure. This procedure is then repeated using a 2 μℓ spike of calibrating solution which is twice the concentration of the first spike. Again it is important to emphasize that signal integration must be employed in computing the signal values for these runs.

2.4 Proposed Procedure for Gas Chromatography

Turn on argon and oxygen gas flows to the flow rates given in Table 3. Preheat the injection valve and transfer line. Inject 10 μℓ of the sample solution into the GC using a gas tight syringe. Initiate the thermal program given in Table 3. Record the signal over a period sufficient for the complete removal of compound electron is Me_3SnPe, Me_2SnPe_2 and $MeSnPe_3$. Measure the peak area of each compound.

2.5 Interferences (ETV Investigation)

Mass spectral overlap interferences are much less severe than optical spectral overlap, particularly when plasma sources are employed. In ICP/MS the most serious interference problem appears to be ionization suppression.

2.5.1 Ionization Suppression and Vapourization Interferences

All elements, present in significant amounts in a sample, can potentially cause ionization suppression problems. Those with ionization potentials below 8 eV are of greatest concern in this regard.

When the matrix substances are present to the point that they significantly increase the electron density in the ICP or significantly reduce the argon reagent ion levels, they can affect the analyte ionization and hence the signal. Since the typical electron density or total ambient ion density in the axial channel of the plasma is 10^{15} cm^{-3} [5], when the number density of easily-ionizable matrix atoms in the axial channel approaches this value, the degree of ionization of the analyte atoms becomes much lower than that without the matrix elements. The amount of an easily ionized element which will cause this problem has been found to be 1 μg (Na). This matrix effect in the ICP is often termed a plasma loading interference.

It is important to separate out the plasma loading interference from other matrix effects of the ETV/ICP/MS combination. To do this an ETV was designed similar, in all respects, to the single filament one [5], except that 2 filaments were installed side by side. In this way separate aliquots of matrix and analyte could be vapourized simultaneously. Thus 1 ng analyte elements and 1 μg matrix elements could be vapourized simultaneously from two adjacent filaments and their signals compared with those from vapourization from the same filament.

Results of such investigations for a variety of analyte and matrix elements have been previously obtained and will appear in detail in an upcoming publication [8]. For the elements of interest in this study, Cu, Pb and V, both vapourization and plasma loading interferences were identified when ng levels of analyte were vapourized in the presence of μg levels of matrix elements.

2.5.2 Compound Formation

Compound formation on the filament volatilizer is suggested by the appearance of multi-peaked signal tracings. (Another possible cause of double peaks could be that the analyte element is absorbed on the filament surface in 2 different states having different desorption energies.) Multi-peaked signals have been noted by many researchers, particularly in furnace atomic absorption work. In some cases the compound formed can be identified from the analyte appearance temperature. In practice, low heating rates are helpful in studying this phenomenon because they permit more clearly-resolved peaks. Conversely, very high heating rates tend to obviate this effect, a finding which is very important for quantitative analysis using the ETV/ICP/MS system.

Examples of compound formation involving the analyte and the Re filament (e.g., Se) and the analyte and sample matrix constituents (e.g., V with Cℓ) have been noted. In addition, Cℓ (a common matrix constituent) interaction with the Re filament was a serious problem. (See acid-anion interferences below.)

2.5.3 Anion Interference

Real sample solutions at their final volumes must contain 1% acid concentration to ensure stability of trace elements in solution. Thus anion(s) associated with acid(s) are present at relatively high concentration. Acid effects have been demonstrated for conventional ICP/MS systems (i.e., those which involve aspiration of the sample solution into the ICP). Effects, particularly from P, S and Cℓ, containing anions can be severe [9]. Sample introduction by ETV has a potential advantage over such systems. With the ETV the sample can be dried and ashed prior to introduction, thus allowing removal of excess acid anion. Also if matrix modification is used the identity of the remaining anion (i.e., that bound to the analyte and remaining matrix) can be changed if desired. Because of the well known adverse properties of phosphate anion on the ICP/MS system [9] no investigation of this anion was attempted.

The effect of different anions on copper signal was studied, first, when the molar ratio of Cu to anion was 1:1 no adverse effects on the copper signal were noted for chloride, nitrate, sulfate or acetate. When Cu solutions were made up with 3% and 6% acid (concentrations commonly used in ICP optical emission) serious anion effects were found for both concentration levels (greater detail will appear in Park et al [5]). Results show that both peak height and peak area reductions occur. A greater problem occurs with the higher acid content (6%). In all cases sulfuric acid gave the largest signal reductions. Depending on the element varying magnitude of signal decrease was noted for the other acids.

In many cases the magnitude of signal reduction also varied with the final Re filament temperature. For example, with nitric acid a lesser Cu peak height reduction occurred for higher filament temperatures. The opposite was true with hydrochloric acid.

The observed peak height and peak area reductions may be due to two factors:

(1) The acid-anions lower the desorption rate (reduces peak height and broadens peak).

(2) The acid-anions cause an increase in Re loss from the filament which results in plasma loading (decreases peak area).

One of the potential davantages of the present system over direct insertion using a wire loop is the capability for controlled temperature ashing investigations. Preliminary ashing investigations made to date, without a controlled temperature ramping step show an appreciable improvement (up to 100%) in signals obtained when sulfuric acid was the major acid anion. Lesser improvements were noted in the case of other acid anions. Future studies involving matrix modification and slow temperature rampings to the final ashing temperature will be done. This approach should be particularly useful in removing chloride (e.g., add NH_4No_3 to remove chloride as $NH_4C\ell$).

The following generalizations are important at the present state of ETV methods development:

(1) The anion effects on the analyte signal are negligible when the anion concentration is not significantly higher than the analyte concentration. Therefore, for maximum sensitivity, acid solutions of the lowest possible concentration should be used in preparing the sample solutions.

(2) To avoid gross systematic errors when calibrating by the standard addition technique, both sample and reference solutions should be made from the same kind of acid solutions and hae the same final acid concentration.

It is of interest to pursue the ossible use of high levels of chloride to improve the volatility of metals during the volatilization step (many metals from chlorides which have boiling points in the 0 to 800°C range). To investigate the possibility of signal enhanced in the presence of chloride, the levels of this element must be much higher than would be achieved at normal acid matrix concentrations. In this regard $\mu\ell$ aliquots of solutions of $MgC\ell_2$ as varying concentrations up to saturated solution levels were added to the aliquot of metal on the Re filament. Results show that a significant improvement in peak height for all the elements studied (Pb, Cu and V) may be achievable. However, the ultimate magnitude of this improvement was masked by a deleterious plasma loading effect resulting from the increased loss of Re from the filament. Very preliminary data obtained from a graphite fibre filament suggests that this approach may be quite fruitful. Hence future investigations with magnesium chloride solution on metal volatility from the graphite fibre filament will be made.

A new programmable ETV power supply is almost completed. This device will allow the use of a wide range of temperatures and heating rates for drying, ashing and vapourizing. In this regard our experiences with the present manual adjustments of temperature and only one choice of heating rate suggests that problems of sputtering and popping of samples and incomplete matrix modifications obtained during drying and ashing should be largely overcome with the use of the programmable supply.

2.5.4 Matrix Spectral Interferences

When solution nebulization is employed several potential interferences involving species of oxygen, nitrogen and hydrogen are possibly in the mass spectrum. The use of an electrothermal vapourizer minimizes such a problem.

The most severe mass spectral interference noted, to date, in these investigations was Zn^{64} on Cu^{63} and Cu^{65}. With the present instrument it was not possible to use a resolution good enough to eliminate the problem. Thus, under best conditions, it was found that 1 μg/mℓ Zn generated a signal equivalent to about 62 ng/ℓ of Cu.

2.6 Calibration (ETV Investigation)

If possible, it was desirable to construct a calibration graph from signals obtained by running simple dilute acid calibrating solutions. The signals obtained from the samples are then compared with those obtained from the calibration graph to give the solution concentration for the sample. It was found, however, that such an approach yielded erroneous results for several types of samples. Thus the method of 'standard additions' was used for quantitative work. Signal integration was used for all determinations.

2.7 ETV Operational Parameters

The ETV presently being used has no capability for adjusting the temperature ramp during drying, ashing and vapourization cycles. Thus as touched on above, considerable problems with sample decrepitation were encountered.

The drying step in particular is very sensitive to the speed of temperature rise. It is desirable to employ a slow (20 to 30 sec) ramp from room temperature to 100°C to ensure no sputtering. In the work to date, sputtering was frequently noted during the dry cycle.

The ashing step provides the opportunity to remove troublesome matrix ingredients. Little success has been achieved to date, in this regard, again mainly because the present power supply was so inflexible. Experiments with matrix modifiers such as NH_4NO_3 to remove chloride were largely fruitless. Losses of volatile analyte and analyte halide were frequently encountered even at power supply adjustments which should give filament temperature below critical volatilization temperature. This was probably due to momentary temperature overshoot.

The ash step is important for the removal of organic matter. Under the present conditions encrustations on the Re filament of black residues were common even after the ash step. To aid in the ashing of organic material, investigations were carried out to determine if oxygen could be utilized in the carrier gas stream, during the ash step. Unfortunately, this resulted in a rapid deterioration of the Re filament. The use of oxygen during ashing will be investigated further with the graphite filament.

Flow rate of the carrier gas through the ETV is a very critical parameter. For the elements studied to date, a value of 4.0 ℓ/min was found to be optimum. For example, when the flow rate reached 5.5 ℓ/min, the signal has been reduced to less than 10% of its optimum value. Surprisingly, with the 3 dome sizes (increasing volumes above the filament by 2 and 6 times), there was no appreciable change in the optimum (4.0 ℓ/min) and limiting (5.5 ℓ/min) flow rate requirements.

The permissible compositions of the filament are of great importance. Metal filaments have the advantage that the power supply can be relatively simple and small in output. In addition, it is easy to cut and form them into a useful geomery. Of the suitable metals only Re proved to combine good forming characteristic with durability under most conditions. However, when volatilization temeprature of 1900°C and above are required even Re is not satifactory. For this purpose graphite has been chosen and details of its characteristics and utility will appear in the next report.

2.8 Plasma Power

An incident power of 1.25 KW was used throughout this work. At higher powers the analyte signal increased significantly but this was counter-balanced by an increase in background signal.

2.9 Operation of ICP/MS for GC Detection (Chromatography Investigation)

The ICP was run in a very similar manner to that used for the ETV work. However, when argon alone was used in the chromatograph and as the carrier gas, a large carbon buildup occurred on the outlet of the sample uptake channel. This resulted in very poor detection limits and deteriorating plasma stability. To overcome this problem, it was necesary to add oxygen to the carrier gas. This was done by installing an oxygen inlet in the heated transfer line. The oxygen flow rate was adjusted to just completely eliminate the carbon deposit (10-20% of total gas flow). The oxygen flow rate required depended on the identity of the solvent being used.

A plasma incident power of 1.25 KW was found to be optimum for this application. The tuning conditions for the oxygen-argon plasma were quite different from those for a purely argon plasma.

3.0 RESULTS

3.1 Determination of Cu and Pb in SRM's (ETV Investigation)

3.1.1 Analysis of Solutions

A variety of biological and environmental standard reference samples were analyzed using the proposed procedure. Copper and lead results are given in Table 4. Vanadium determinations were also attempted. However, further investigations of the graphite filament vapourization will be necessary before quantitative results can be obtained for vanadium.

Table 4. Values Obtained for Cu and Pb in SRM's

MESS-1	21±2 (25±3.8)*	34±1 (34±6)
BCSS-1	22±1 (185±2.7)	21±2 (23±3)
Tomato L	10±2 (11±1)	6.1±2 (63±0.3)
Tort 1	431±39 (439±22)	11.0±2 (10.4±2)
River Sed.	112±6 (109±19)	714±35 (714±28)
Coal Fly Ash	96±10 (118±3	70±3 (72.4±0.4)
Urban Particulate	624±120 (609±27)	TH

*Certified value. TH - too high for ETV.

These results are preliminary as significant improvements are to be expected with use of the programmable power supply. In spite of this, the results obtained for Cu and Pb show an acceptable agreement with the certified values in the majority of cases.

Several other elements have been determined in a few of these samples. However, these results are not recorded here because the list of samples analyzed is very incomplete and there are few and, in many cases, no certified values for these elements in the standards.

3.1.2 Direct Analysis of Solids

The ultimate goal of this research is to develop the capability to directly analyse solids (i.e., without need for chemical sample preparation). In this regard, it was of interest to attempt an early run to look for major problem areas which could be developing.

NBS Bovine Liver Powder was slurried with water and a 2 $\mu\ell$ aliquot dispensed onto the Re filament. The following thermal program was employed: dry at 150°C (30 sec), ash at 800°C (30 sec) and vapourize at 1950°C (3 sec). During the dry and ash stages, decrepitation of the sample occurred. Also the peaks obtained for Cu and Pb were broader than is desirable. This means that ashing must be more complete and that the vapourization temeperatures should be higher. Using the Re filament it is not ossible to use a higher temperature. Thus further work on direct solids analysis must await the programmable power supply and further investigation of the graphite filament.

3.2 Separation and Determination of Tin Compounds (Chromatography Investigation)

At this oint no results have been obtained on real samples. Synthetic mixtures of the three tin compounds of interest (Me_3SnPe, M_2SnPe_2 and $MeSnPe_3$) were chromatographed using the proposed chromatographic conditions and procedure. Chromatographic peaks showing good resolution of the 3 compounds were obtained. Table 5 lists the retention times and best detection limits obtained at this time.

Table 5. Retention Time and Detection Limit Data

	Retention Time (sec)	Detection Limits (ng)
Me_3SnPe	74	6
Me_2SnPe_2	95	16
$MeSnPe_3$	134	10

Detection limits obtained by Chau et al [10] were 0.1 ng for each compound. Because of problems with our prototype ELAN, the signals obtained in any investigation are between 10 and 100 times poorer than the commercial instrument. Taking this into account our detection limits for these preliminary investigations are quite good for this early stage in the investigation.

4.0 CONCLUSIONS

(1) Two sample introduction systems for ICP/MS were studied:

   (a) An electrothermal vapourizer (ETV) was evaluated for the introduction of liquids and solids. The elements Cu, Pb and V were investigated.

   (b) A gas chromatograph was interfaced to the ICP/MS and the separation and determination of alkyltin compounds was studied.

(2) ETV results:

   (a) An Re filament was used in the determination of Cu and Pb in a variety of standard reference samples. (Vanadium could not be determined using the Re filament because of its low volatility and the severe plasma loading problem which occurs when Re is used at temperatures above 1900°C)

   (b) The results obtained for Cu and Pb in the standard reference samples were, for the most part, in acceptable agreement with certified values.

   (c) A carbon filament is being investigated for the determination of Vanadium. Early results suggest a marked improvement in signal shape and magnitude for this filament.

   (d) Ionization suppression interferences and anion interferences were found to occur in the ETV approach. However, controlled programs for drying and ashing (used together with matrix modifiers) which will soon be available to us will allow suppression to some degree of these problems.

   (e) Mass spectral overlap interferences can also be encountered with this approach. However, since air and water are excluded from the ETV simple introduction system, a simpler pattern of such interferences is obtained compared to nebulization sample introduction. The most serious spectral overlap problem encountered to date was the slight overlap of Zn^{64} with Cu^{63} and Cu^{65}. A correction was made for this problem.

(f) Operational parameters and ETV Figures of Merit:

- Ar flow through ETV chamber should be 4.0 ℓ/min.
- Incident plasma power 1.25 KW (reflected power near zero).
- Sample size, up to 5 μℓ (of slurried solid or sample solution).
- Re metal filament can be used to 1900°C, carbon filament to 2500°C (estimate).
- Method of standard additions used for calibration.
- Transport efficiency for Cu and Pb better than 80% (solutions of analyte plus dilute acid).

(3) Gas chromatographic results.

(a) Compounds separated were Me_3SnPe, $MeSnPe_2$ and $MeSnPe_3$ (Me = methyl and Pe = pentyl) using a 3% OV-1 on Chromasorb W (80-100 mesh) column.

(b) Operational parameters of importance are:

- Flow rates: Ar - 8 ℓ/min
  O_2 - 2 ℓ/min (introduced in transfer line)
- Temperatures: Injector, 250°C
  Column, 60°C to end of peak (1) and 250°C to end of chromatogram
- Plasma incident power, 1.25 KW, reflected power near zero.

(c) When Ar is used alone in the system, carbon deposits, which trap Sn, occur in the torch and orifice. Thus oxygen must be introduced into the transfer line.

(d) Results obtained:

- Elution order of compounds $MeSnPe_3$, Me_2SnPe_2 and Me_3SnPe.

- Retention times in sec and (detection limits in ng) 74(6), 95(16), 134(10).

5.0 ACKNOWLEDGEMENT

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DEVELOPMENT OF SELENIUM ANALYSIS METHODOLGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION

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ABSTRACT

Our studies of nutritional factors important in controlling the composition of phytoplankton populations have indicated that some phytoplankton species in softwater lakes subject to acidic precipitation require the element selenium for growth. Some of these phytoplankters produce undesirable blooms. The levels of selenium required by these species is low. However, the meagre data available on Se concentrations in softwater lakes indicate that Se levels may be low enough to limit the growth of some phytoplankton, and that Se inputs from acidic precipitation, a known source of Se, may affect the composition of these communities. Because of the dearth of data on Se levels, it was decided to apply a sensitive method to analysis of this element in soft waters. In addition the known effects of Se in ameliorating some of the toxic effects of Hg suggest that Se may be important in soft waters for other reasons.

Atomic absorption methods as conventionally applied yield a detection limit in the µg/L range. This is inadequate for the studying the levels normally encountered in softwater lakes. A gas chromatographic method was applied and allowed detection at the low ng/L level. Several new features of this method have not been used previously in analysis of Se in natural waters. These include application of capillary chromatography to analysis of the piaselenol derivative (of 4-nitro-o-phenylenediamine) in soft waters, and a single flask derivatization procedure which reduces handling and potential contamination. Retention time of the piaselenol peak was about 1.8 min with total analysis time of 5 min, at an operating temperature of 250 °C. Preliminary data indicate that Se concentrations vary with season and depth and are typically less than 1 µg/L in softwater lakes. The method can also be used to study the distribution among the various species (Se^{IV}, Se^{VI} and organoselenium).

INTRODUCTION

The element selenium was discovered by J. J. Berzelius, a Swedish chemist, who in 1818 scraped it from the walls of vats in a sulfuric acid plant (Oldfield 1981). This early observation anticipated our current interest in Se in relation to the emissions of SO^{2} which give rise to acidic precipitation. It has long been known that Se accompanies sulfur as an air pollutant emitted as a result of the combustion of coal (Cooper et al. 1974). This is the single most important source of atmospheric Se, contributing more than 60% of the Se emitted to the atmosphere, exceeding the amount from metal smelting (primarily copper) the second most important source (National Academy of Sciences Committee 1976). The comparison between total natural emissions and anthropogenic emissions of Se is poorly explored, but the best current estimates indicate that the emissions due to industrial activity (e.g. coal burning and copper smelting) exceed natural sources by at least 5-fold or as much as 34-fold (Galloway et al. 1982). Also, Se (along with As) is particularly enriched in power plant emissions compared to other elements (Chadwick and Lindman 1982). Evidence from sediment cores indicates that an increase in Se deposition, presumably due to atmospheric emissions has occurred since the 1950's (Heit et al. 1981). Most inorganic Se is probably insolubilized in the sediments (Turner and Rudd 1983). However, some may be resolubilized in an organic form (Cutter 1982).

Our specific interest in Se was stimulated by our observation that Se is absolutely required for growth in culture by Chrysochromulina breviturrita (Wehr and Brown, 1985), a phytoplankter which causes undesirable blooms in lakes subject to acidic precipitation. Even at 100 ng Se/L yield was doubled over the controls. Also experiments at the Experimental Lakes Area (Kenora, Ont.) indicated that addition of electrolyte grade sulfuric acid (contaminated with Se) to lakes resulted in a C. breviturrita bloom.

A review of the literature on Se requirements by phytoplankton revealed evidence for its essentiality in several marine species of Chrysochromulina (Pintner and Provasoli 1968), a freshwater dinoflagellate Peridinium cinctum fa. westii (Lindstrom and Rodhe 1978, Lindstrom 1983) and a freshwater diatom Stephanodiscus hantzschii var. pusillus (Lindstrom 1983). Subsequent subculture in Se-free media resulted in no growth (Wehr and Brown 1985). The results significant in the laboratory context. However, the key issue is the relation between Se and phytoplankton blooms. Se from coal-fined combustion arrives at these remote areas by "episodic precipitation" (Parekh and Husain 1981), e.g. air masses which receive plumes from coal-fined power plants have sporadically high Se concentrations. We suggest that this episodic precipitation which is high in Se may give rise to C. breviturrita blooms on a sporadic basis. This would account for the unpredictable pattern of bloom occurrences observed by Nicholls et al. (1982). To test this hypothesis, environmental concentrations must be measured and the values applied in continuous culture. The present work deals with this problem, and will enable us to assess the role of Se in phytoplankton ecology.

LITERATURE REVIEW

The major problem has been an unsatisfactory detection limit (e.g. 1 ug/L Se) at the various laboratories which sometimes do Se-analyses. The most sensitive and specific method that has been applied to water samples involves measurement of the amount of the 5-nitropiazselenol derivative by electron capture-gas chromatography (Measures and Burton 1980a,b). This method is specific for Se and has been reported to provide a detection limit of 0.8 ng/L for marine waters (Measures and Burton 1980a). Seawater Se concentrations range from 20-180 ng/L (Measures and Burton 1980a), and some data indicate that Se in fresh waters are below 100 ng Se/L (Suzuki et al. 1981). In highly contaminated lakes within the vicinity of Sudbury, concentrations range between 100-400 ng/L (Nriagu and Wong 1983), but no data exist for less contaminated lakes. These levels are well below the level of detection by the conventional AA or ICP methods currently used.

MATERIALS AND METHODS

a. Chromatography. A capillary splitter (J & W Scientific) was installed in a Varian 3700 gas chromatograph. The column of choice was a 0.2 mm (15 m) OD fused silica column (DB-5) from J & W Scientific operated isothermally at 250 °C with a flow rate of 1.5 mL/min and a split ratio of 100:1. See also Table 1.

b. Sample bottles: Linear polyethylene (LPE) or high density polyethylene (HDPE), Nalgene 500 mL size.

c. Acid washing of glassware:

1. Soak several hours to overnight in 10% HNO_3
2. Rinse at least 5x in purified (reverse osmosis) water
3. Rinse at least 5x in glass-distilled or other high quality water.

d. Acid for preservation: 1 mL of concentrated HCl per 500 mL of lakewater (more acid may be needed for high alkalinity waters). Final pH should be within the range of 1.8-2.0 with this acid addition.

e. Filtration: (as needed for evaluation of "soluble" i. e filterable Se). We have used primarily 0.45 µm pore size Millipore cellulose acetate filters, prerinsed 5x with glass-distilled water in an acid-washed beaker. Nucleopore (polycarbonate) filters can also be used. An all glass filtration with glass-fritted and silicone bung (or all-glass unit) is recommended.

f) Derivative formation: (adapted from Measures and Burton 1980a): The reagent is 1.0 % 4-nitro-o-phenylenediamine (Aldrich Chemical Co.) (NPDA) in 10% HCl added at a rate of 2 ml per 100 mL of sample in a 100 mL volumetric flask capped with a teflon-faced, rubber-lined screw cap (Pyrex brand). This was allowed to react in subdued light for 2 h. A 1mL aliquot of toluene (glass-redistilled) is addded and the mixture is shaken vigorously 25x by hand (ca. 3 min). This single container system has a considerable advantage over previous methods (e. g. Measures and Burton 1980a) which require separatory funnels and transfers of samples with the risk of both loss of samples and contamination. Layers are allowed to separate and the toluene layer removed with a toluene-washed (10x) pasteur-pipette to a 1 dram pre-washed glass vial with a teflon-lined cap (Supelco Canada Ltd. Catologue # 2-3288). Samples prepared in this way can be stored at least 6 months at -20 °C without degradation.

RESULTS AND DISCUSSION

a. Capillary chromatography. To our knowledge all of the previously reported work (Dilli and Sutikno 1984) has been with packed columns with their inherently lower resolution compared to capillary columns. It seemed a worthwhile objective to develop a capillary based system for these analyses especially in view of the fact that chromatograms for most of the previously reported work have not been particularly clean.

Our first attempts with a capillary type system has been with a megabore (large internal diameter) column, J&W Scientific DB-WAX (15 m). This column proved to be a poor choice as the Se-derivative (piaselenol) and the unreacted derivatizing reagent appeared to react with the column liquid phase giving a very poor chromatogram from the view of sensitivity and resolution.

The next column tried was another fused-silica megabore column, J&W DB-1 (15 m). This column has a relatively nonpolar methyl-siloxane bonded liquid phase (similar to an Se-30 silicone gum). It provided resolution of close to the level of the packed column work in the literature. We observed, however, a small neighboring peak which appeared to interfere with quantitation of the piaselanol. Our attempts to resolve this peak from the piaselenol by temperature programming were not successful. At this point it was decided to convert the chromatograph from a packed column instrument to full split capillary configuration. An inlet splitter (J&W Scientific) was installed on the inlet end and a fused silica capillary detector insert (Varian Instruments) was installed on the detector end of the Varian 3700 chromatograph. A comparison of chromatograph performance with regard to resolution and retention time is given in Table 1. After conversion to capillary operation the instrument was fitted with a J&W DB-5 fused silica column (15 m) which is a somewhat more polar phenylmethylsiloxane bonded liquid phase. Consequently, the retention time of the piaselenol was increased, and this necessitated higher column temperatures to keep retention times within practical limits (Table 1). This system provided us with a good compromise of resolution and analysis time, and appeared to be free of any problems associated with interference from any neighboring peaks.

b) Results with the DB-5 capillary system: sample chromatograms and standard curves. A typical chromatogram is given in Figure 1. The piaselenol provides a fairly sharp peak at about 1.8 min with a variety of other peaks representing byproducts of reaction or the unreacted 4-nitro-o-phenylenediamine (NPDA) derivatizing reagent (2.4 min). The analysis time is somewhat limited by this large peak of unreacted material. However, the time (approximately 5 min) when run isothermally (Fig. 1) is consistent with the handling of large numbers of samples especially if autoinjection equipment is used. Presently, we are investigating the possibility of reducing the amount of NPDA to further minimize the effects of the presence of this peak. Preliminary results have indicated that reducing the concentration of this reagent by 50% has no measurable effect on the size of the piaselenol peak.

Figure 2 indicates the detector response is linear within this range, and we estimate a working detection limit of 5 ng/L which has been adequate to evaluate all samples from softwater lakes thus far analyzed. We have tended to prefer peak height to area as a measure of concentration as this was somewhat less sensitive to interference by peaks generated by reaction byproducts. Precision of analyses for both standards and field samples on both peak height and peak area basis is provided (Table 2).

c) Effect of acid concentration on piaselenol chromatography. The most obvious effect of varying the piaselenol concentration is in the size of the NPDA peak which increases at low acid concentration (Fig. 3). However, high acid increases the size of the piaselenol blank, thereby increasing the effective detection limit. It is preferable to limit the magnitude of the blank, so the lowest possible acid concentration is recommended.

d) Analyses of environmental samples. Environmental samples from Lake 302 South of the Experimental Lakes Area presented a more complex sample matrix than the laboratory standards with an obvious increase in the number of peaks (Fig. 4). This increase in the number of peaks did not cause any obvious problems in data analysis, but may cause problems with other sample matrices. Data from Lake 302 South is plotted in terms of concentration (Fig. 5). Concentrations vary from 100-800 ng/L which is well above our detection limit of 5 ng/L, but at or below the limit of the conventional atomic absorption method. It is apparent that a hypolimnetic increase in Se^{IV} occurred during stratification. It is not clear, however, whether this is common in softwater lakes as we believe these are the first data of this kind produced. Concentrations in euphotic zone appear to be below 200 ng/L. These levels would likely be limiting to the growth of some phytoplankters based on our previously reported findings (Wehr and Brown 1985).

e) Continuing work. This project is continuing in the areas of Se speciation with particular emphasis on extending the assay to Se^{VI} and organsoselenium which may exist in these waters. Also we need more information on sample storage and stability and any possible interfering compounds which may be encountered as we broaden the range of waters examined.

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Table 1. Comparison of selenium analysis with "Megabore" and capillary chromatography columns under various temperature programs.

Column	Column Pressure (lbs/in2)	Initial temp. (oC)	Prog. rate (oC/min)	Final temp. (oC)	Se peak retention time (min)	Total analysis time (min)	Cooling time (min)	Relative resolution
Megabore DB-1	5.0	150	none	150	3.4	12.0	none	good
		170	none	170	1.6	9.5	none	fair
		190	none	190	1.1	8.0	none	poor
		200	none	200	0.8	6.5	none	poor
		120	25	190	2.8	10.0	2.5	good
Capillary DB-5	11.0	190	none	190	6.5	12.5	none	excellent
		230	none	230	3.1	6.8	none	excellent
		250	none	250	1.8	5.0	none	good*
		180	10	250	4.7	8.0	2.0	excellent

*recommended method

Table 2. Precision of injected samples (5 uL each) on DB-5 capillary column compared on the basis of peak height and area. Field data was from Lake 302 South, Experimental Lakes Area, Ont. (1985).

Sample	n	peak height			peak area		
		$\bar{x}$	SD	CV	$\bar{x}$	SD	CV
Standards							
100 ng Se^{IV}/L	14	9333	513	5.5	628	82	13.0
250 ng Se^{IV}/L	3	23673	60	0.2	1210	108	8.9
Lakewaters							
L 302-S; 8 Jun 8 m	5	17827	1496	8.4	1287	270	21.0
L 302-S 1 Aug 1 m	4	14460	1726	11.9	1105	234	21.2
L 302-S; 23 Oct 8 m	6	15777	656	4.2	1110	372	33.5

Fig. 1 Typical chromatogram for analytical standard (100 ng/L Se^{IV})

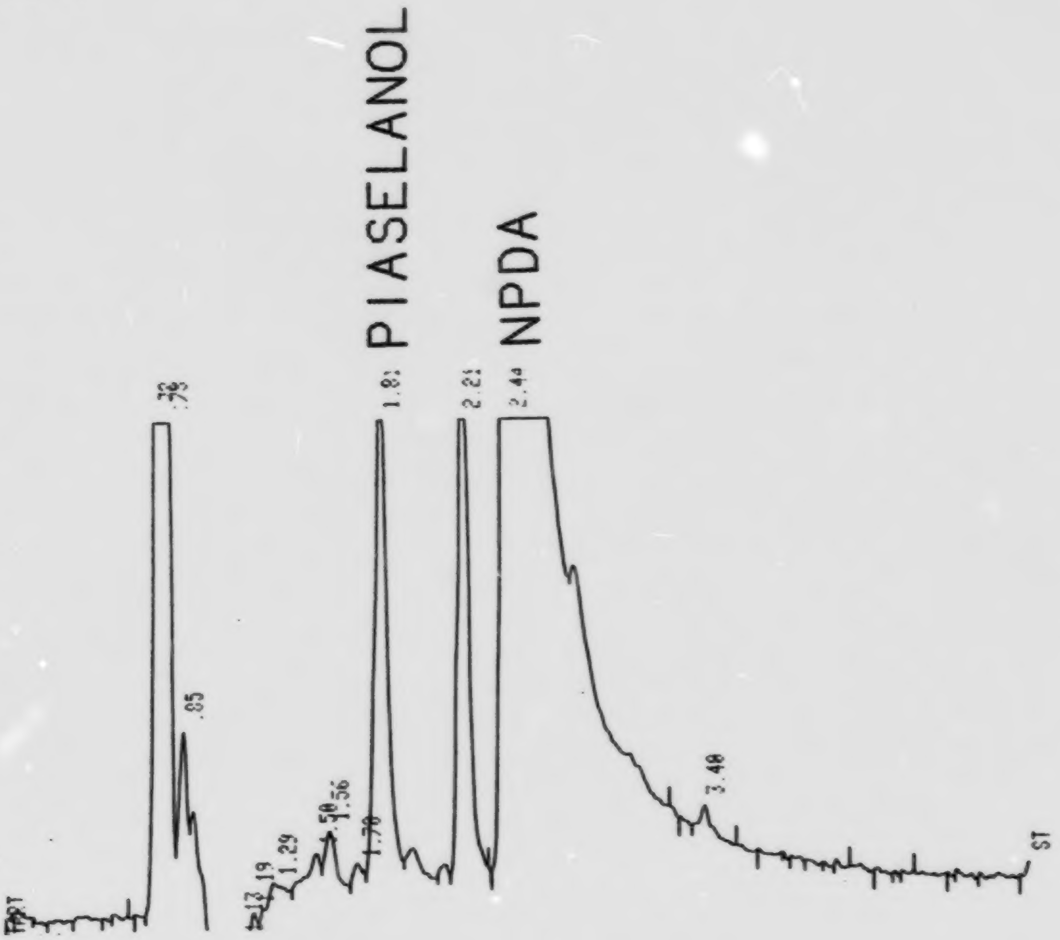


Fig. 2. Standard curve of piaselenol derivative of Se^{IV} as measured by capillary chromatography (peak height basis)

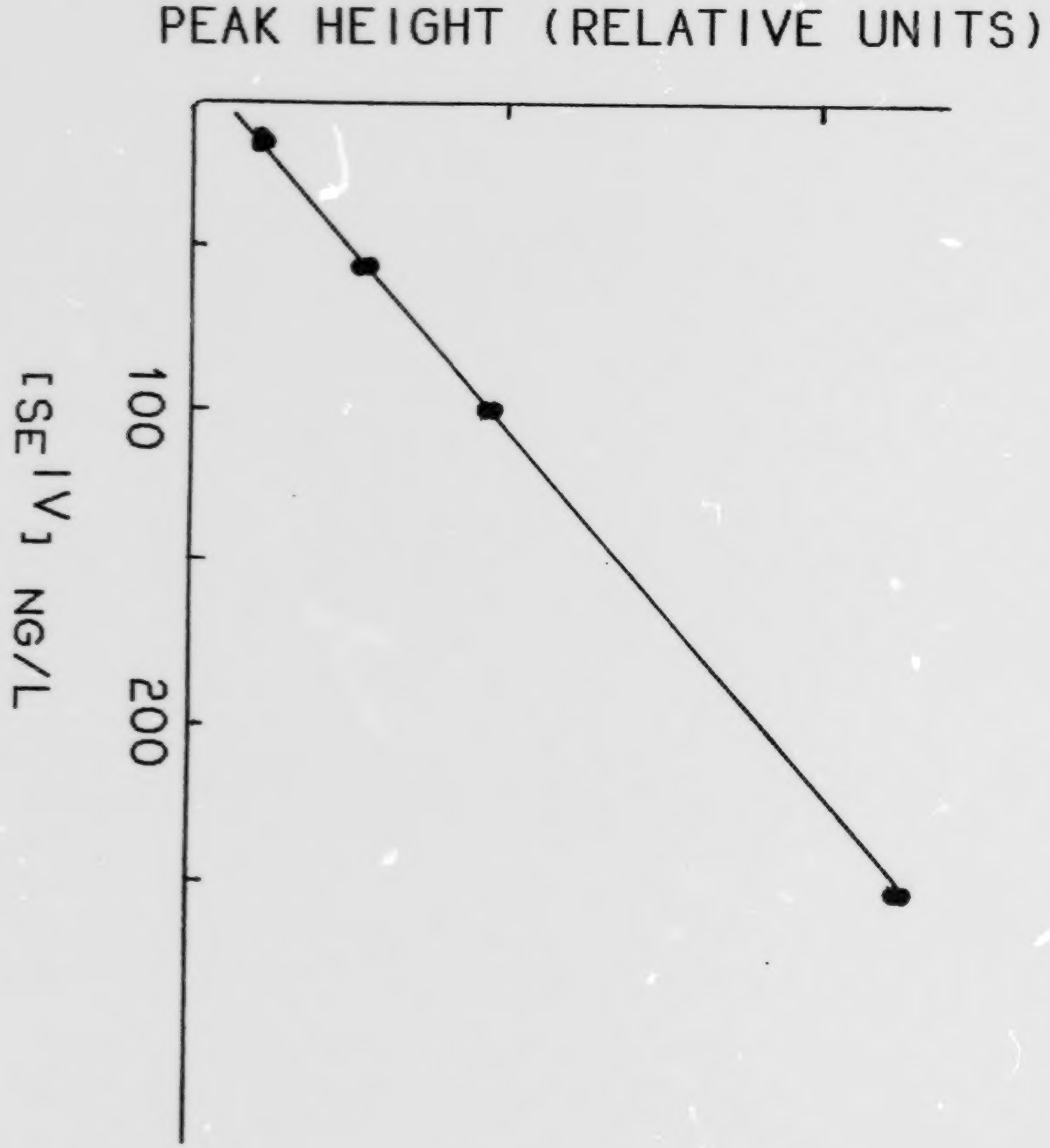


Fig. 3. Blank for standard curve at 0.01 M HCL (low acid)

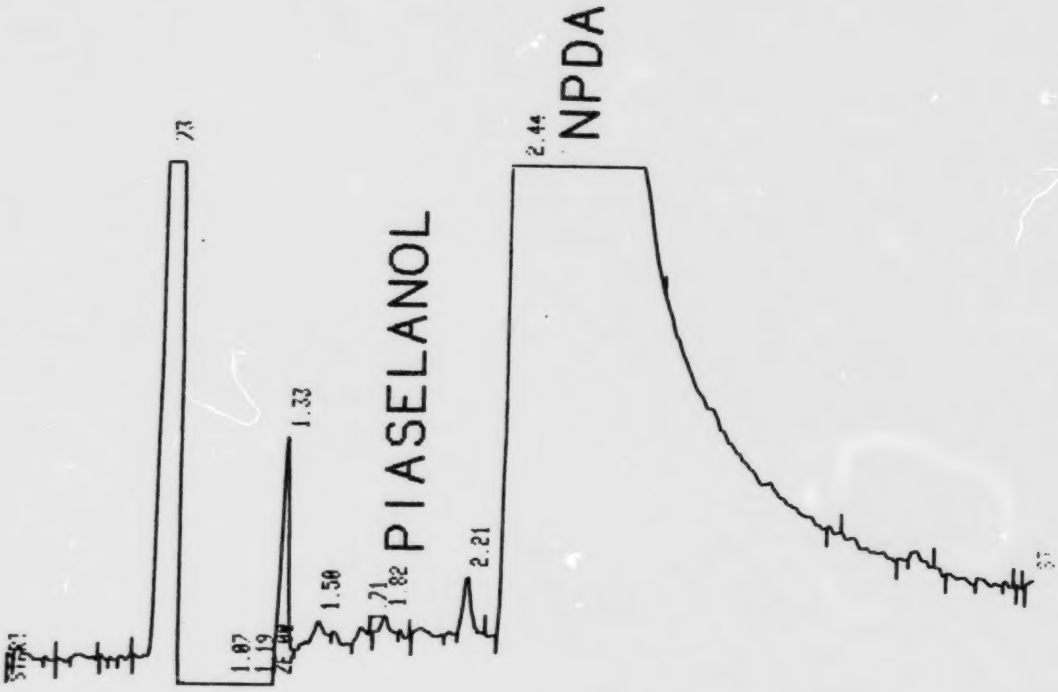


Fig. 4. Lake 302-S, Se^{IV}, Aug. 27, 1985, 1 m.

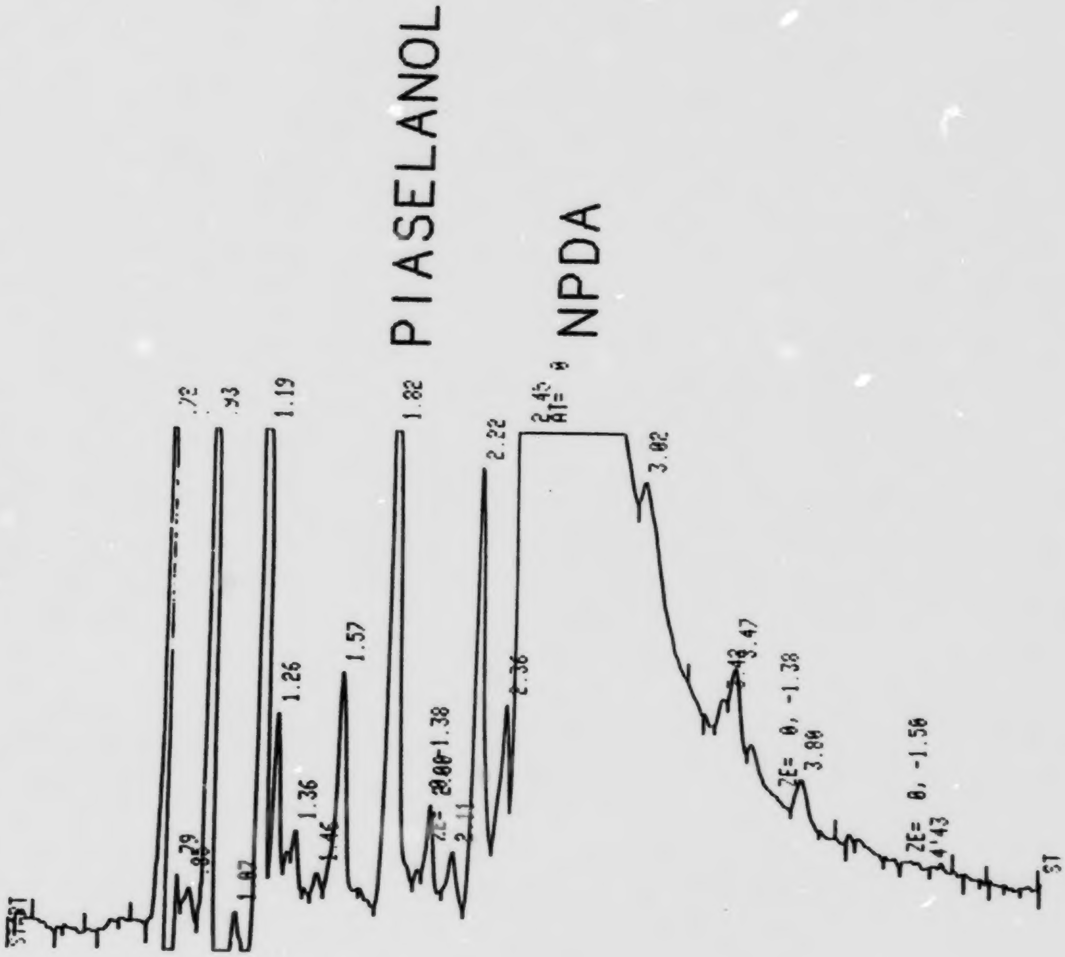
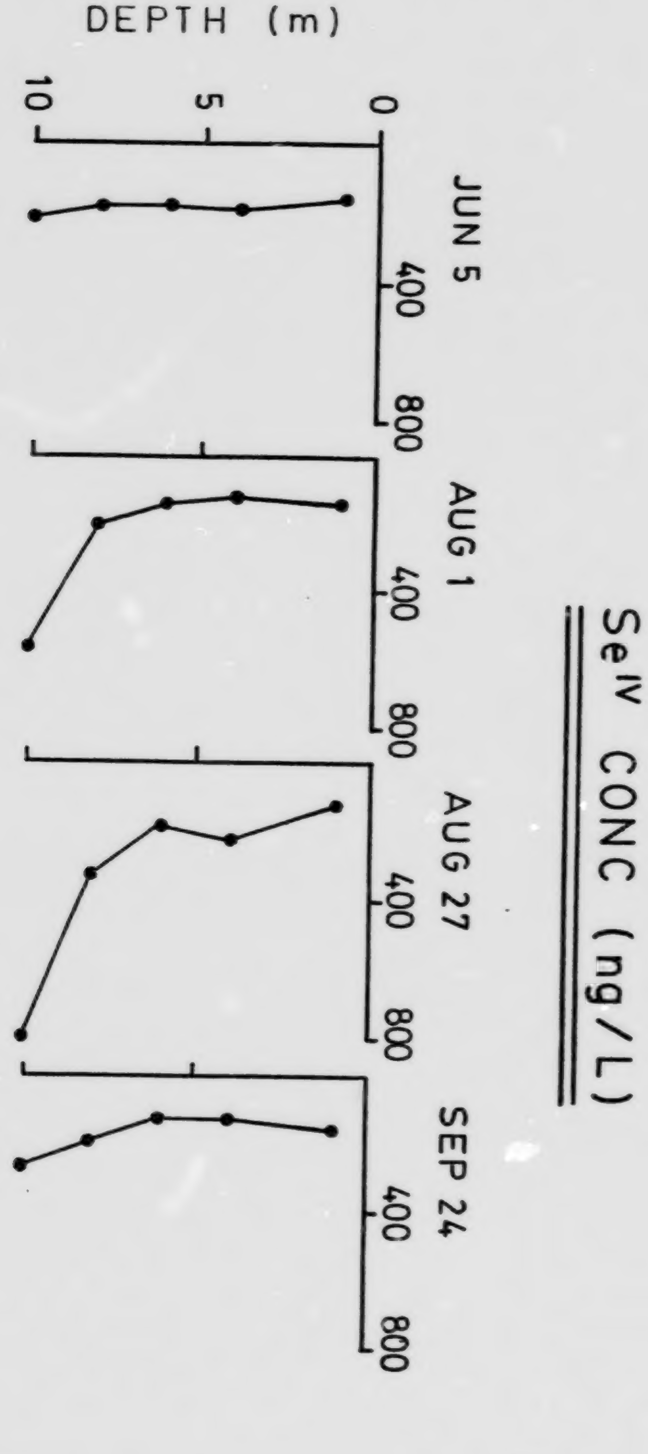


Fig. 5. Seasonal and depth variation of Se^{IV} in Lake 302-S as measured by the gas chromatographic method (1985).



EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION

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Paper not received at print time

DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS

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Ontario Ministry of the Environment

1. Introduction

The nebulization of samples is of central importance in atomic spectroscopic (AS) analysis. It has long been known that the conventional method of pneumatic nebulization is a far from efficient (6%) means of aerosol production for AS analysis [1]. Ultrasonic nebulization (USN), on the other hand has proven since 1964, to be a more efficient (86%) means of sample introduction [2].

Despite its seemingly superior efficiency, USN has yet to gain widespread acceptance. Many researchers however, report a variety of inadequacies with USN [3-9]. These include: 1) relatively poor short and long term stability, 2)longer clean-out times, 3) excessive long term drift, 4) memory effects and 6) high cost. Documented evidence shows [10-14] that continuous flow USN with desolvation offers a number of advantages over pneumatic nebulization as a means of sample introduction into the analytical ICP. The literature records many with descriptions of applications of USN to some of the most difficult analytical tasks encountered by the analyst [15-21].Two recent commentaries however, have presented a more balanced view on the present status of USN. Barnes [21] has concluded that "full advantage of these nebulizers has not been taken by most ICP users. This is expected to change as the properties of the USN-ICP combination with practical samples are fully described." Thompson and Walsh [8] projected that the above deficiencies "could be improved upon by careful attention to details of design."

Early research in this laboratory has engendered a feeling of optimism in the potential of USN. It is now believed that by proper redesign of the system and consideration of the limiting variables, such as stable and reliable transducer operation and 'proper' aerosol transport, a reliable and analytically useful USN could be developed.

2. Experimental

Schematic diagram of the USN design (as of date of writing manuscript).

Figure 1. Schematic diagram of ultrasonic nebulizer with desolvation.

Sample solution is pumped onto the water cooled transducer (a) with a peristaltic pump (Multistatic, peristaltic pump-HAAKE BUCHLER Instruments Inc.) via the sample inlet (b). The Ar carrier gas introduced through the drain tube (d) carries the aerosol through the heated tube (e) and condenser (f). The carrier gas plus sample is then directed into the plasma.

The power supply is a modified version of the BIONAIRE BT-200 ultrasonic humidifier (BIOTECH Electronics Ltd., Quebec, Canada). Specifications of modified and unmodified power supplies are given in Table 1.

To date, several condenser designs have been utilized or are under consideration. These include:

1) Freidrichs condenser
2) Cleisen condenser
3) Double surface Davies condenser
4) Modified Graham's condenser similar to that described by Olson et. al. [4]

Preparation of Fassel type [22] transducer assembly.

Using Kelvin's equation (1), and assuming that for aqueous solutions the product-quotient $\frac{8\pi\sigma}{\rho} = 0.1515$, and for a driving frequency of 1.68 MHz, then λ is calculated to be 0.3772 cm. Therefore, the thickness of the quartz plate is given by $\Phi = \lambda/2 = 0.1886$ cm. A small amount of bonding agent (Eccobond 55/Catalyst #11- W.R. Grace & Co., Burlington, Ont.) is placed between the transducer and the quartz plate. Bonding is effected by applying gentle pressure with the thumb and index finger, taking care that all air bubbles are excluded from the bond.

Tests were also done using polymers to coat the transducer working surface, instead of a quartz plate. Table 2 lists the polymers employed with the corresponding solvents.

The transducers were cleaned ultrasonically by immersion in aa approximately 0.0007% detergent solution (Actionox, American Scientific Products, McGaw Park, IL) for 15 minutes, followed by rinsings in isopropyl alcohol and acetone, again ultrasonically for 15 minutes. Immediately prior to application of the polymer coating, the transducers were placed in a beaker saturated with isopropyl alcohol vapour and then allowed to air dry.

With the exception of polyurethane spray, all polymers were applied by dipping the transducer into a solution of the uncured or dissolved polymer. Different film thicknesses were obtained by varying the extent of dilution of the polymer solution.

The various coatings were evaluated based on the duration of adhesion of the coating to the transducer and, sensitivity and stability of the emission signal.

All calibration standards were prepared from serial dilutions of 1000 ppm stock solutions (BDH Chemical Co.). For ICP atomic emission analysis, eleven replicate, one second integrations were done per sample, per analyte.

3. Discussion

The power supply, as supplied, had an output frequency of 1.7 MHz, delivered at a 120 Hz ripple. The average frequency experienced by the transducer was therefore 1.24 ± 0.30 MHz. The addition of a capacitor filter in series with the circuit and then taking the output across the capacitor, resulted in improved average output frequency and increased maximum power (see table 1).

As noted above, the Ag electrodes on the transducer are coated with approximately 1 um of Ni metal, for protection. This type of Ag/Ni working surface leads to serious problems however, as the transducer was manufactured to operate using water and not acidic solutions. Nebulization of slightly acidic soutions (> 1% HNO_3) causes complete dissolution of the Ni and Ag in a matter of one hour or less.

To date, the method used to protect the Ag/Ni transducer working surface from degradation has been to bond a quartz plate over it. The thickness of the plate can be calculate from Kelvin's equation

$$\lambda = \left\{\frac{8\pi\sigma}{\rho f^2}\right\}^{1/3} \qquad (1)$$

where λ = wavelength (cm) of capillary waves
σ = surface tension (dyn/cm) of solution
ρ = liquid density (g/cm^3) of solution
f = driving frequency (MHz)

The quartz plate thickness is then given by

Bonding a quartz plate to the transducer results in several difficulties. Not only is the manual reproduction of the bonding process difficult, but for solutions of different sigma (σ) and rho (ρ), theoretically, the thickness of the quartz plate should also vary. Further, the thickness of the bonding glue layer effectively adds to the solid thickness that the ultrasonic waves must traverse. If this thickness is not totally compatible according to Kelvin's equation, the waves are attenuated (and reflected back onto the transducer) and cause eventual burn-out of the transducer. As seen from table 3, using such a system, set up in this lab, a decrease in analytical performance was observed with time. Thus a new approach was investigated in this work for the protection of the Ag/Ni working surface. That is, to coat the surface with a polymer film.

To date, of the polymers investigated, only the polyurethane polymers and Aquasil showed any promise. All others dissolved within 15 minutes of initiating operation with 1% HNO_3. One other polymer being considered is a combination of two polymers (D.E.R. 331 and D.E.R 736, Dow Chemical Co., Sarnia, Ont.). This mixture has proven resistant to 2% HNO_3, under operation, for a minimum of 4 hours. It has not however, been fully investigated. Table 4 gives a comparison of results obtained with pneumatic nebulization and ultrasonic nebulization utilizing Fassel's system, no coating and Aquasil coating on the transducer surface.

Production of aerosol at the transducer surface is a function of many parameters. The ones of primary importance are the liquid film thickness on the transducer surface, the viscocity of the solution (salt content), the applied oscillating frequency, the transducer temperature and the amplitude of the applied power. Even if one assumes that the viscocity, applied oscillation frequency and applied power remain constant, one cannot make the same assumption of the liquid film thickness on the transducer surface or the transducer temperature.

The transducer temperature is directly dependant of the power applied, amount of solution coming into contact with the working surface and the cooling water flow under the transducer. (To a lesser extent also to the power reflected and the oscillating frequency). Assuming the applied power is maintained at an essentially constant level, then under optimum operating conditions, one can regulate the cooling water flow and other parameters to such an extent that the transducer temperature no longer is a variable in the production of aerosol.

However, the liquid film thickness on the working surface is still a problem. And, it is not one that can be readily or directly eliminated. But, there is an indirect method of compensation. This is, the automatic control of the applied power in response to variations in aerosol production efficiency due to variations in the surface liquid film thickness. A new power supply is being developed with a feedback system, set up to respond to differences in aerosol density passing a unit area at the inlet to the heated tube.

4. Results

As can be seen from plots I-IV, linear calibration curves were obtained for Co, Cu, Fe, Mg and Zn. Also, table 5 shows good agreement between accepted values and those obtained by the method proposed above, for the analysis of NBS sea water.

Table 6 gives a comparison of detection limits for the Meinhardt and Ultrasonic nebulization.

Table 1

Power supply specifications

Unmodified supply	
Average output frequency	1.24 ± 0.3 MHz
Maximum power	50 W
Modified supply	
Avegrage output frequency	1.68 ± 0.01 MHz
Maximum power	75 W

Table 2

Polymers used and corresponding solvents or solvent mixtures

Polymer	Solvent(s)
PC 29, a polyurethane based circuit board coating (Dexter Hysol, Toronto, Ont.)	MEK
Polyurethane spray	---
Aquasil, a hydrophobic polymer (Chromatographic Specialties)	---
Polymethylmethacrylate	MEK toluene/acetone
Polystyrene (Aldrich Chemical Co.)	MEK
Polyethylene	toluene/acetone
Silicone rubber	n-heptane

Table 3

Sensitivity as a function of time with Fassel's system

Cu sensitivity* (ppb)	Time (hrs) of operation	RSD (%) for 2 ppm Cu
16	0	3.5
21	2.5	3.7
29	5.5	3.3

* Concentration required for 0.0044 absorbance

Table 4

Comparison of results for various systems

Type of system	Cu sensitivity* (ppb)	RSD
(1) pneumatic	87	0.8
(2) Ultrasonic (no coating)	15	1.8
(3) Ultrasonic (Aquasil)	11	0.6
(4) Ultrasonic (Fassel [25])	16	3.5

Table 5

Comparison of experimental and accepted values for the analysis of NBS sea water.

	Concentration (μg/L)		
Element	this method	NBS certified	RSD(%)
Co	28.6	26 ± 1	1.4
Cu	24.7	21.9 ± .4	2.1
Fe	98.9	99 ± 8	1.2
Zn	71.6	66 ± 2	3.1

Table 6

Comparison of limits of detection

	LOD (μg/L)	
Element	Meinhardt	USN*
Co	3.4	0.70
Cu	2.3	1.07
Fe	1.2	0.31
Mg	13.7	2.40
Zn	4.0	0.88

* With desolvation

Table 7

Ultrasonic nebulizer operating parameters

Sample flow rate	6 mL/min
Ar carrier gas flow rate	0.95 L/min
Max. forward power	75 W
Oscillating frequency	1.68 MHz

Table 8

Transducer Specifications

Dielectric	Bi/Tc
Load	50 Ohms
Operating Frequency	1.68 MHz
Electrodes	Ag
Protective coating	Ni

Table 9

Heated tube specifications

Quartz	
Length	12 cm
Inner diameter	10 mm
Electrothermal heating tape (Canlab)	100 W
Temperature	80 - 200 °C

Table 10

ICP operating parameters

Model	ARL 34000 ICPAQ
Incident power	1600 W
Reflected power	< 3 W
Plasma gas	0.8 L/min
Coolant gas	12 L/min
Observation height in coil	15 mm

Table 11

Analyte lines used

Element	Wavelength (nm)	Order
Co	228.62	2
Cu	324.75	2
Fe	259.94	2
Mg	279.08	2
Zn	213.86	3

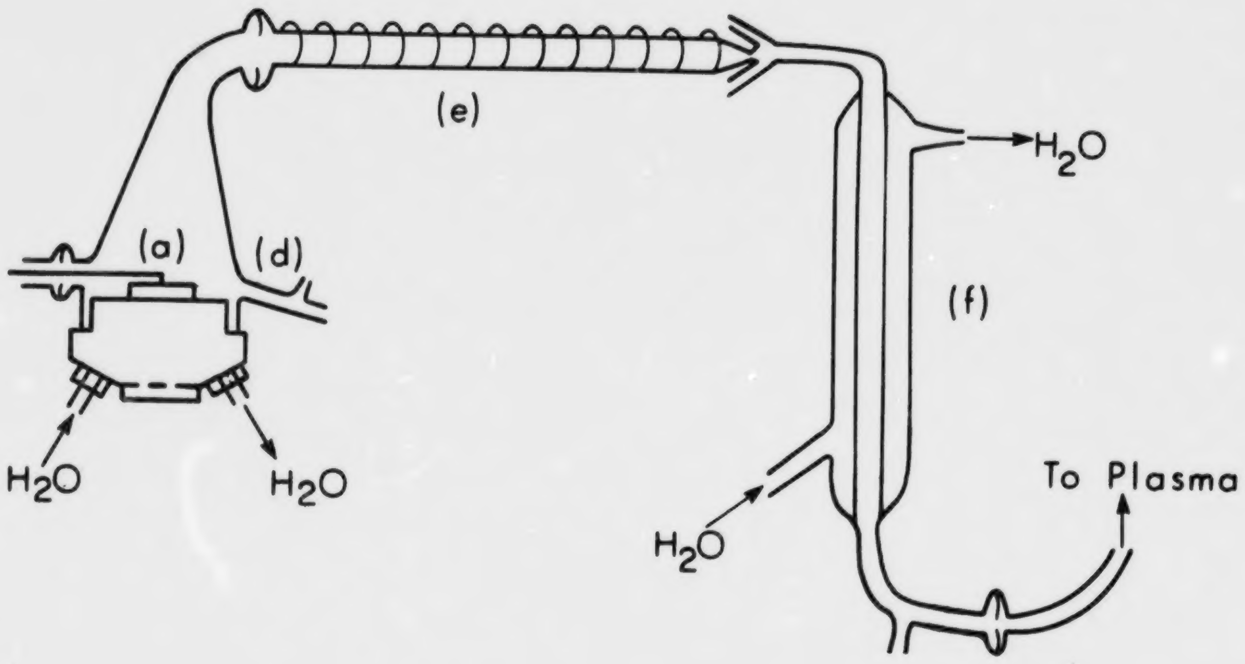
(a)
(d)
(e)
(f)
H_2O
H_2O
H_2O
H_2O
To Plasma

FIGURE 1

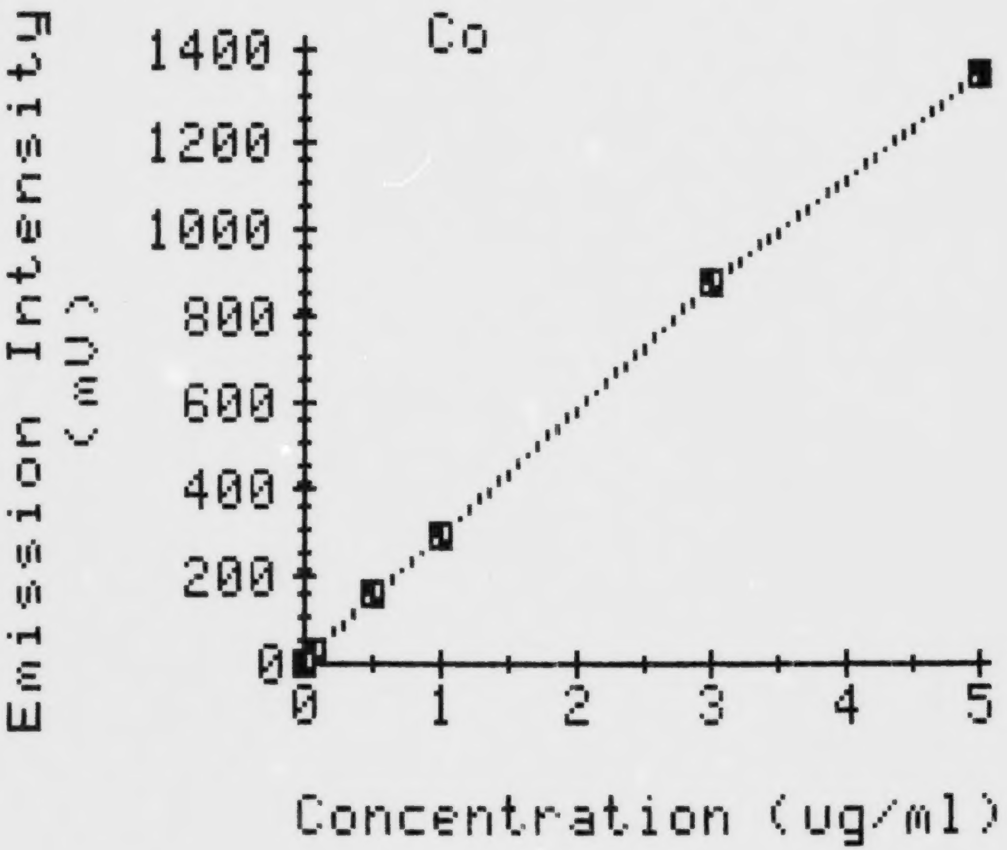

Figure 2: Calibration plot for Co.

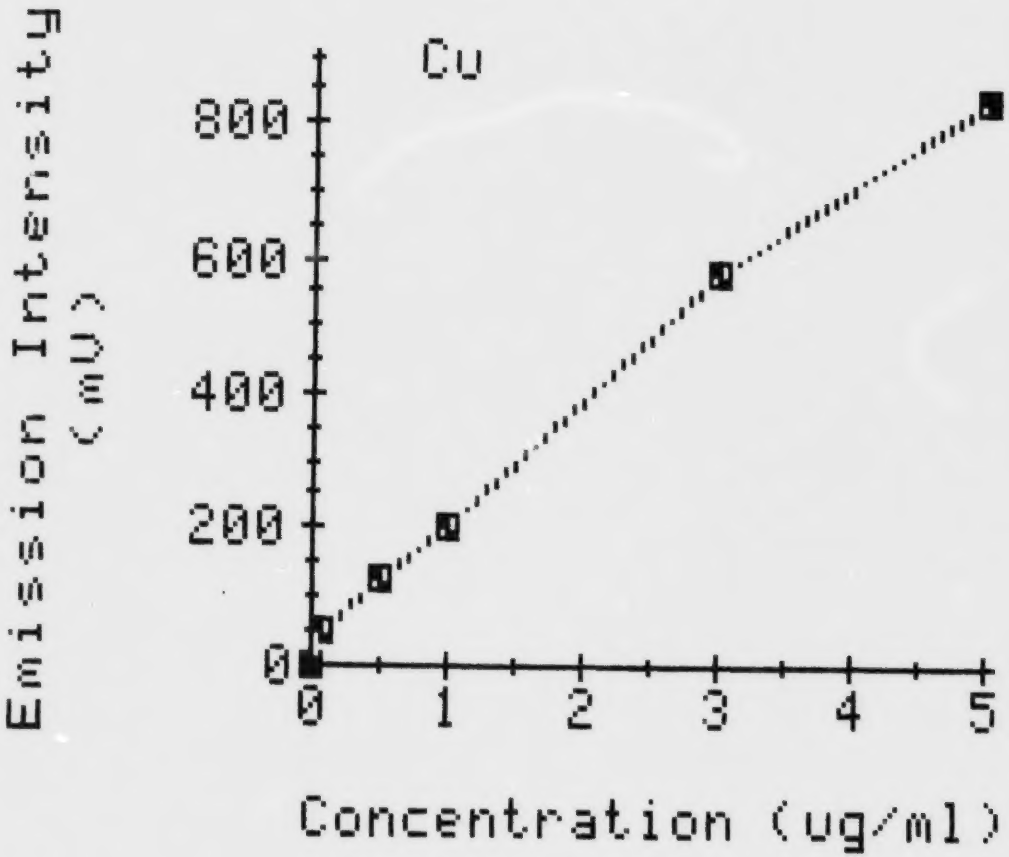

Figure 3: Calibration plot for Cu.

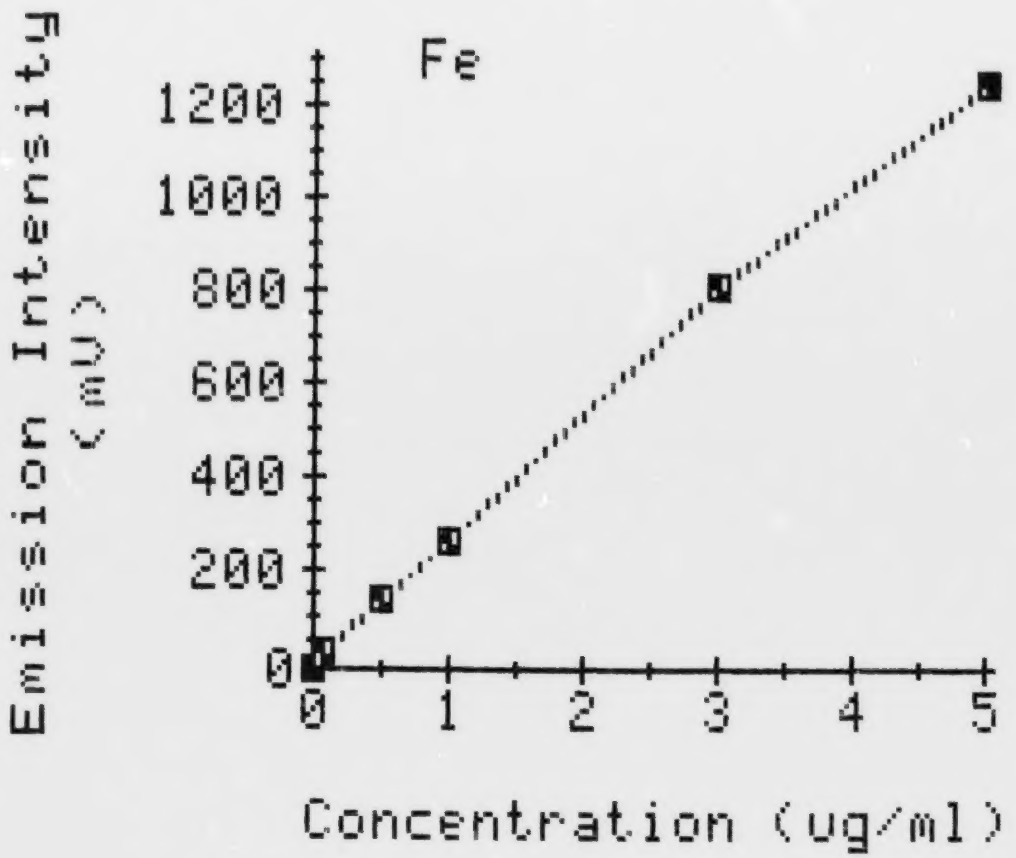

Figure 4: Calibration plot of Fe.

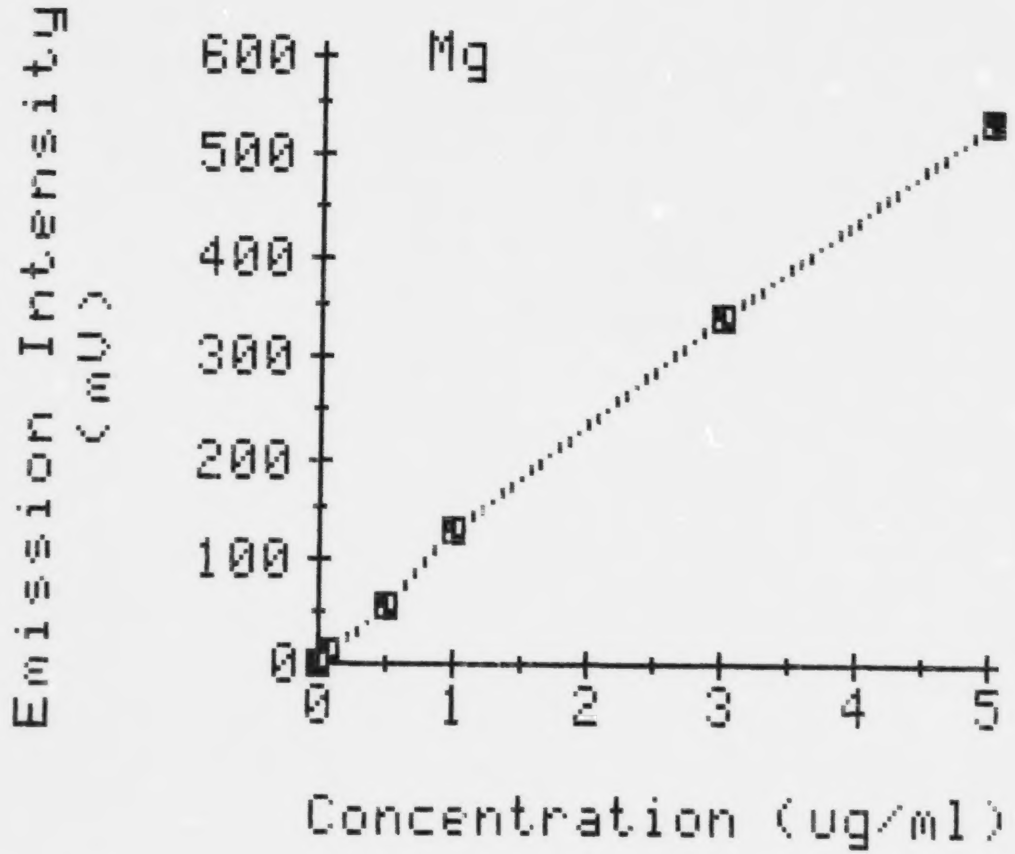

Figure 5: Calibration plot for Mg.

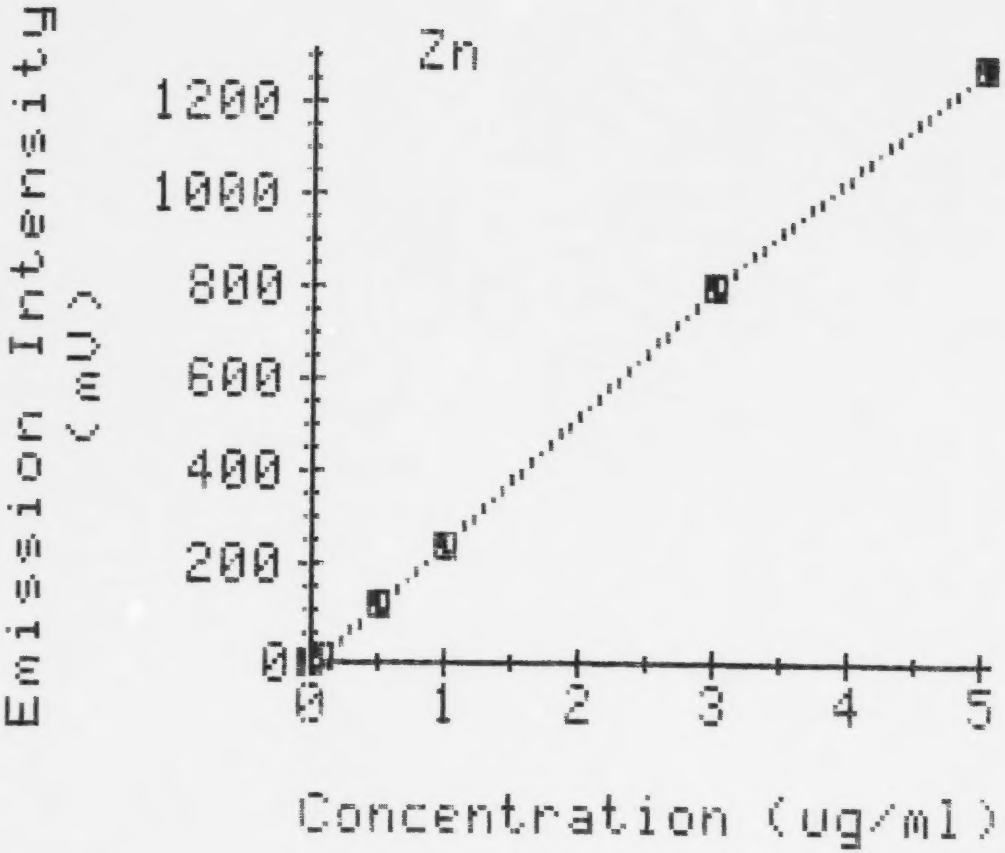

Figure 6: Calibration plot for Zn.

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Development of Recombinant DNA Probes to Determine the Origin of Fecal Streptococci at the Toronto Area Beaches

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Abstract

Total cellular DNA from fecal Streptococci from goose, human and gull origin were digested with restriction endonucleases. The digestion patterns were grouped into families by visual inspection for commonality. An isolate from goose feces was chosen as a candidate for preparing the goose probe because this "family" included both sediment and fecal isolates.

The total cellular DNA was digested with the restriction endonuclease Bam HI and inserted into the Bam HI site of the cloning vector pUC 9. The colonies of E. coli which had been transformed by a recombinant plasmid were screened for plasmid content. The plasmids were digested with Bam HI and electrophoresed in agarose gels. The DNA was transfered to millipore membranes (Southern blots) and probed with 32-P-labeled total cellular DNA from Streptococcus faecalis var liquefaciens of human origin.

An insert of 6.6 Kb which did not hybridize to the probe was chosen as a candidate for the goose streptococcal DNA probe. This plasmid was radiolabeled with 32-P and used to analyze the total cellular DNA of fecal Streptococci of goose, human and gull origin.

The probe hybridized to the "family" of goose fecal DNA from which it was derived and not to the human fecal streptococcal DNA of non-laboratory workers. In addition only one the twenty (1/20) gull isolates reacted positively.

In a similar manner a probe for human fecal streptococcal DNA was generated from Streptococcus faecalis var liquefaciens of human origin and candidate recombinant plasmids were selected by their inability to hybridize with the total cellular DNA of Streptococcus var liquefaciens of gull origin. A plasmid with an insert of 2.0 Kb was found to react with four of twenty (4/20) fecal streptococcal DNA of human origin but not with any of goose or gull origin.

Introduction

The recent increase in the closing of Toronto's public beaches has been in response to high fecal coliform and fecal streptococcal counts. Although these assays are useful indicators of the presence of water-borne pathogens, they provide little information on the source of fecal contamination. Based on the fact that Fecal Coliform:Fecal Streptococci Ratios (FC:FS) vary between human and animal feces, an attempt has been made to use this assay to trace sources of fecal contamination (1,2,6). However, it has been shown that these ratios are highly unreliable due to the different survival capacities of fecal coliforms and fecal Streptococci in differing, especially urban water environments.

Furthermore, the close association between humans, gulls, geese and other animals along the Toronto waterfront has shown that there is a high degree of similarity between intestinal flora of these organisms. A cumulation of these problems has emphasized the fact, that at present there is no reliable method to trace the source of the fecal contamination.

Studies at the DNA specific level exploiting restriction endonuclease analysis (REA) and DNA-DNA hybridization techniques may be the key to defining streptococcal organisms that are host specific. In this study we have attempted to identify specific DNA probes that can distinguish between human and non-human fecal contamination. Such specific DNA probes can be used to assess the contribution of each source of fecal contamination along the Toronto waterfront.

Materials and Methods

Bacteria. Isolations were performed according to the standard bacteriological methods recommended for these organisms (6). These organisms were identified by the API system and included fecal isolates from humans and gulls (Table 1 and 2).

Chromosomal DNA preparation. Streptococcal chromosomal DNA was prepared as previously described (3).

Restriction enmdonuclease digestion of DNA. Approximately 1.0 to 2.0 ug of streptococcal DNA sample was used for each restriction endonuclease digest. The DNA was digested according to the supplier's specifications (Boehringer-Mannheim, St. Laurent, Quebec) except 10 to 20 U of enzyme were used per ug of DNA.

Gel electrophoresis and photography. Sample preparation, the conditions of agarose gel electrophoresis and photography of the resultant restriction patterns were performed as previously described (3).

Cloning procedures. Streptococcal chromosomal DNA was purified and cloned into a pUC-9 plasmid vector according to the method previously described (9,10).

Preparation of 32-P-labeled DNA probes. Duplex DNA samples were labeled with radioactive deoxynucleotide triphosphates by nick translation as previously described (4). The specific activities obtained were routinely 10^8 cpm/ug of DNA. The labeled probes were used within one month of preparation.

Southern transfer and hybridization to 32-P-labeled probe DNA. Southern (8) blotting experiments were performed according to methods previously described (4).

Results

Total cellular DNA from fecal Streptococci from goose, human and gull origin were digested with restriction endonucleases. The digestion patterns were previously grouped into families by visual inspection for commonality (15). An isolate from goose feces identified as Streptococcus durans (#181 strain) was chosen as a candidate for cloning procedures in preparation for its use as a goose probe because this "family" included both sediment and fecal isolates (15).

The total cellular DNA was digested with the restriction endonuclease Bam HI and inserted into the Bam HI site of the cloning vector pUC 9. The colonies of E. coli which had been transformed by a recombinant plasmid were screened for plasmid content. The plasmids were digested with Bam HI and electrophoresed in agarose gels (Figure 1a, 1b and 1d). The DNA was Southern blotted to millipore membranes and probed with 32-P-labeled total cellular DNA from Streptococcus faecalis var liquefaciens of human or gull origin (Figure 1c and 1e).

Thus candidate recombinant plasmids were selected on the basis of their inability to hybridize with the total cellular DNA obtained from human (Figure 1c) and gull (Figure 1e) sources.

An insert of 6.6 Kb (Figure 1a) which did not hybridize to the human or gull probes was chosen as a candidate for the goose streptococcal DNA probe, herein referred to as goose probe #807 (Figure 1c, 1e).

Probe #807 was next radiolabeled with 32P and used to analyze the total cellular DNA of fecal Streptococci of goose, human and gull origin (Figure 2).

The probe hybridized to the "family" of goose fecal streptococcal DNA from which it was derived (Lane 7 in Figure 2a, 2b, 2c and 2d) and not to the human fecal streptococcal DNA of non-laboratory workers (data not shown). However probe #807 reacted with human fecal streptococcal DNA of laboratory workers (Figure 2b and 2d) which suggested the the workers were colonized by the fecal streptococcal strains that they handled in the laboratory. Furthermore probe #807 reacted with only one of eight (1/8) goose restriction families identified in our earlier studies (15) which suggested a high degree of specificity. In addition only one of the twenty (1/20) gull isolates reacted positively (Figure 3).

In a similar manner a probe for human fecal streptococcal DNA was generated from Streptococcus faecalis var liquefaciens of human origin and candidate recombinant plasmids were selected by their inability to hybridize with the total cellular DNA of Streptococcus var liquefaciens of gull origin. A plasmid with an insert of 2.0 Kb was found to react with four of twenty (4/20) fecal streptococcal DNA of laboratory workers (Figure 4b) but not with any of goose or gull origin nor with twenty non-laboratory workers (data not shown).

Discussion

This study extends our earlier observations as to the usefulness of REA or gene fingerprinting techniques for determining the sources and routes of transmission of microbial organisms. In particular we have utilized these techniques for tracing infections (3,5,7,13) and pollution sources (15). Combining cloning and DNA-DNA hybridization techniques we have developed a method whereby unique DNA sequences can be identified that would serve as specific probes for tracing and enumerating the pollution sources in waterways. In particular, we have developed a goose-specific probe which can now be used to enumerate the contribution of goose feces to the over-all bacterial contamination at the Toronto waterfront. In addition we compared results obtained with the goose probe with those obtained from a cloned-fragment probe derived from human streptococci and a gull whole-cell DNA probe.

The results of this study indicate firstly that the goose probe #807 was very specific and did not react with streptococcal strains from non-laboratory workers nor from gulls, but did react significantly with streptococcal strains obtained from laboratory workers. Interestingly, the laboratory workers were involved in the field collections and the testing of the fecal and environmental samples of Streptococci. Thus probe #807 specifically identified a problem associated with this approach, in that lab workers became colonized with the various streptococcal strains handled. On the other hand further tests with the goose probe using streptococcal strains obtained from non-lab workers indicated a complete lack of reaction. From an epidemiological and health point of view these results suggest that fecal streptococcal strains from the waterfront can colonize humans. From a microbiological point of view such human sources should be avoided if attempting to establish types of specific bacteria associated with humans. Thus the probes are only as good as the selection process used to determine a host's microbial flora - "garbage in garbage out".

Secondly, the specificity of DNA probes is crucial and it was for this reason that we initially chose a streptococcal strain that was not the most common strain found in association with goose feces. From this isolate, identified biochemically as a S. durans (strain #181) we obtained the unique DNA fragment for the goose probe #807. If, on the other hand, had we chosen the most common strain found in goose feces as the candidate for development of the probe, a highly specific DNA fragment may not have been elucidated. Based on the suggestion that human sewage is a significant if not the biggest contributor to the overall bacterial pollution at the Toronto waterfront then the most common isolates found in association with either goose or gull hosts could conceivably be of human origin. Thus we sought a less common or more host-specific strain for the development of probe #807.

Thirdly, the technique of genome fingerprinting, combining REA, cloning methods and nucleic acid hybridization techniques, as demonstrated herein, can be used effectively to define the sources as well as the routes of transmission of microbial flora. Presently used conventional techniques based on phenotypic characteristics are unreliable and cannot discriminate strains at the subspeciies level. This is clearly seen by comparing Tables 1 and 2 with the genome fingerprints. In a number of cases strains with identical or indistinguishable fingerprints have been identified by convention biochemical techniques as being different species or subspecies. By comparison the capability of REA and in particular the discriminating power of gene probes to identify minute differences or Restriction Fragment Length Polymorphisms (RFLP's), among otherwise "identical" strains, is remarkable.

The discrepancies between phenotypic-based microbial identification systems and the more novel genetic-based techniques as developed herein is a serious problem in the establishment of useful fecal markers for pollution tracing. Thus our results suggest that a critical examination of the taxonomic relationship among the Group D fecal Streptococci must now be undertaken particularly with respect to their host range, if these organisms are to be used as reliable markers of fecal contamination and standards for water quality assurance. Homology studies should be performed on this large group of organisms in order to establish the most important and unique phenotypic characters that can simply be used to discriminate the various strains.

Similarly, specific fragments of DNA used in these probes can easily be made into expression vectors the protein products of which may be used to developed specific monoclonal antibody probes. Such immunologic-based probes may be more easily adapted to rapid ELISA systems for use at the day-to-day microbiology bench. Our studies are continuing in these directions.

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FIGURE LEGENDS

FIGURE 1:

Selection of recombinant DNA probes for fecal *Streptococci* isolated from geese.

1a. Bam HI digests of pUC 9 recombinant #807 with lambda DNA Hind III digest markers in kilo base pairs (kbp).

1b. Bam HI digests of pUC 9 recombinants of goose fecal *Streptococcus durans* #181 DNA.

1c. Autoradiograph of the DNA transfer (blot) to a millipore membrane of the agaraose gel seen in figure 1b, probed with 32-P-labeled total streptococcal DNA from a human source. The inserts in lanes 1 and 2 (cf black arrows with white arrows in figure 1b) reacted with the probe whereas the fragment in #807 did not.

1d. Additional BamHI digests of pUC 9 recombinants of goose fecal *Streptococcal durans* #181 DNA (including #807).

1e. Autoradiograph of the DNA blotted from the gel seen in figure 1d and probed with streptococcal DNA derived from a gull source. The inserts indicated by black and white arrows indicate reactions with the probe.

FIGURE 2:

Reaction of the goose probe #807 with streptococcal DNA from humans (i.e. laboratory workers), goose, gull and water-sediment sources.

2a. Bam HI digests of streptococcal DNA. Lanes 1 - 6 contain human source (i.e. laboratory workers) streptococcal DNA; Lane 7 contains goose *Streptococcal durans* #181 DNA; Lanes 8 and 9 contain sediment source streptococcal DNA; Lane 10 contains gull source streptococcal DNA.

2b. Autoradiograph of DNA blot from figure 2a probed with goose probe #807 (black arrow indicates the single Bam HI fragment reaction obtained with this probe).

2c. Cfo I digest of the same source DNA as in figure 2a.

2d. Autoradiograph of the 2c DNA blot, probed with #807. Restriction Fragment Length Polymorphisims (RFLP's) are evident in Lanes 5 and 6.

FIGURE 3:

Reaction of the goose probe #807 with streptococcal DNA from gull sources.

3a & 3c. Bam HI digests of streptococcal DNA from gull sources.

3b. Autoradiograph of DNA blotted from 3a and probed with probe #807. Only Lane 1 reacts (black arrow).

FIGURE 4.

Reaction of human DNA probe #1126 with streptococcal DNA from human sources

4a & 4c. Bam HI digests of streptococcal DNA from human sources:

4a. Lanes 1 - 6 = Restriction Family A (see Tables 1 and 2)
Lanes 7 - 8 = Family B
Lanes 9 - 10 = Family C

4c. Lanes 1 - 4 = Family D
Lanes 5 - 6 = Family E
Lanes 7 - 8 = miscellaneous isolates

4b. Autoradiograph of the DNA blot of Figure 4c probes with #1126. Reactions are clearly evident in Lanes 1 - 4.

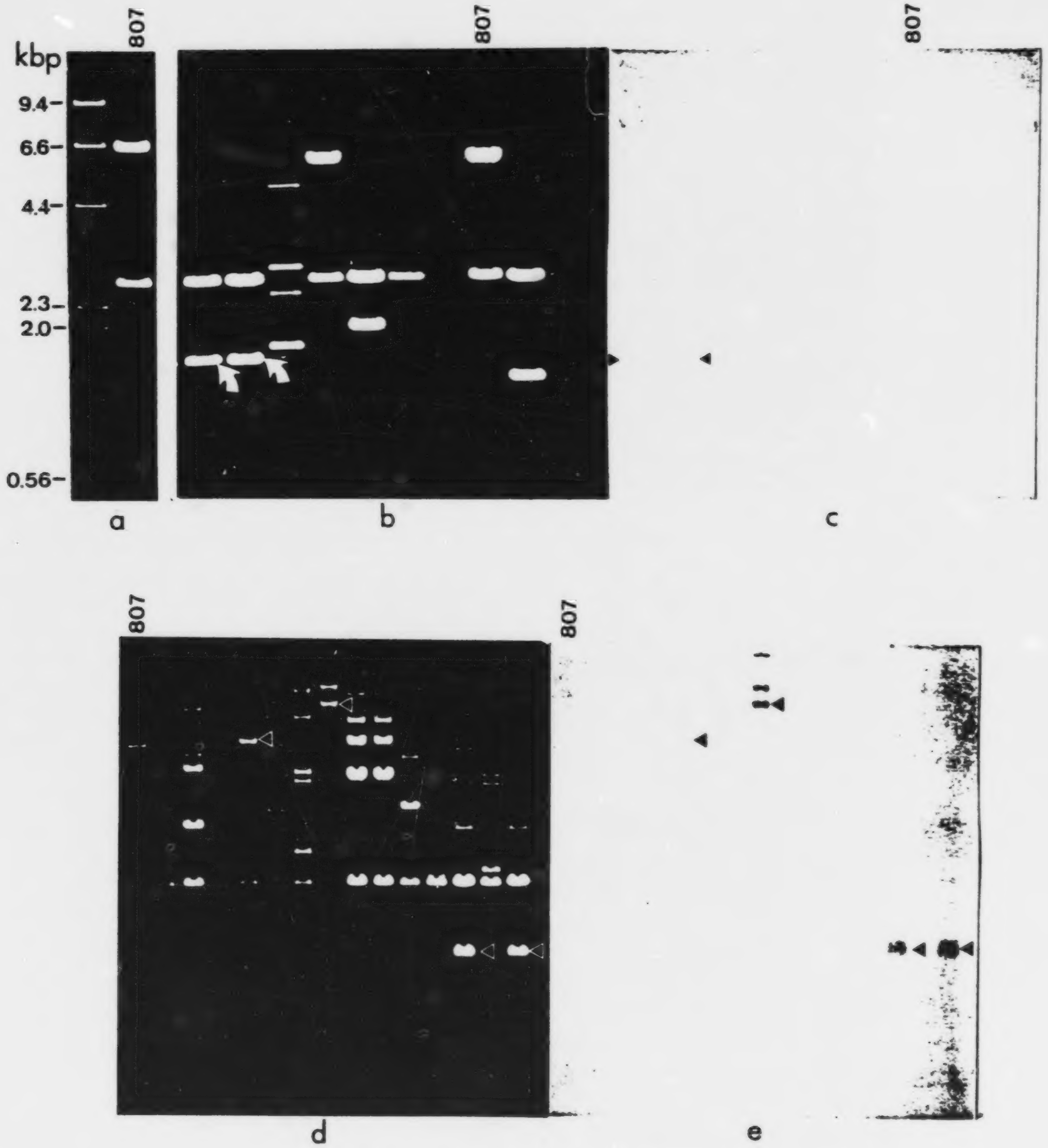
807
kbp
9.4
6.6
4.4
2.3
2.0
0.56
a
807
b
807
c
807
807
d
e

FIG. 1

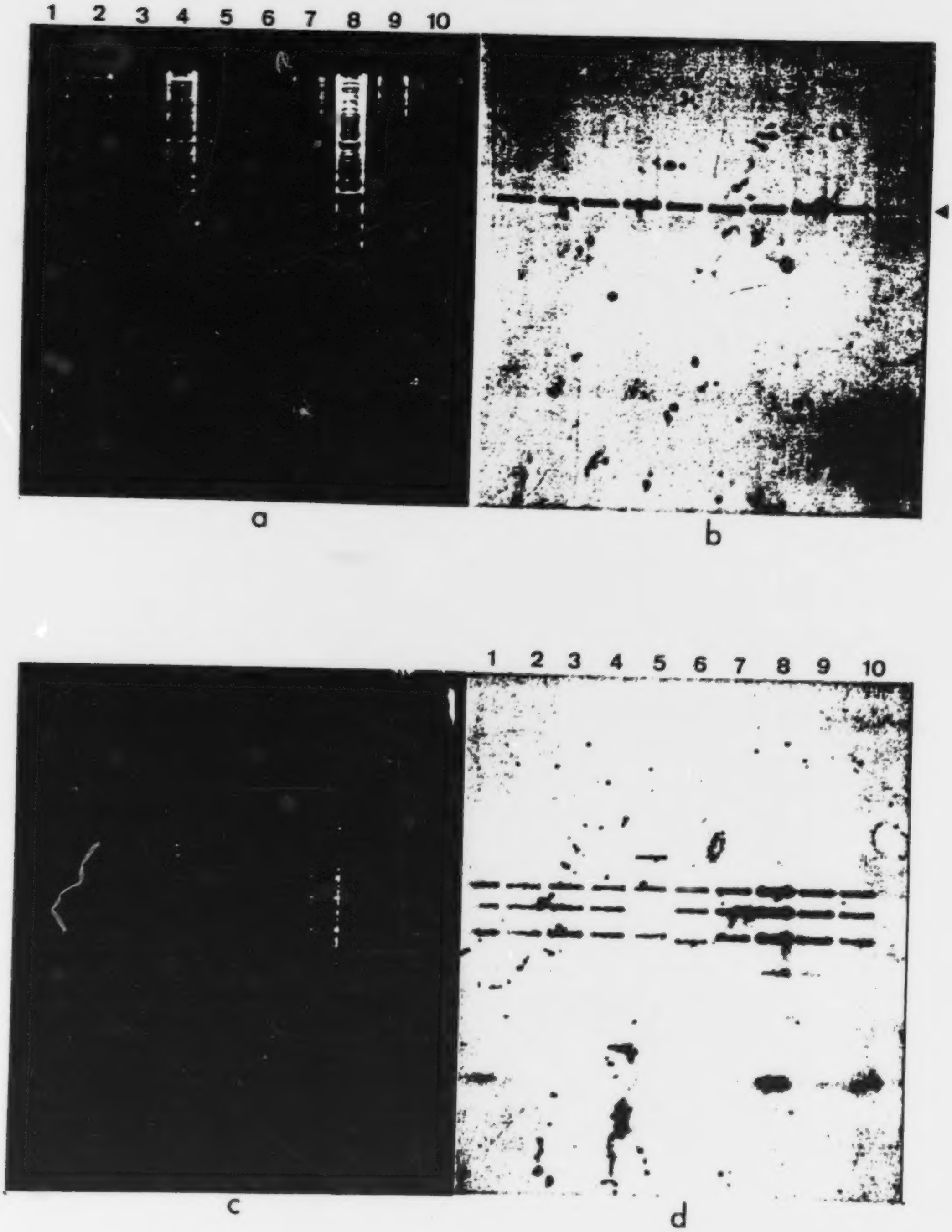
1
2
3
4
5
6
7
8
9
10
a
b
1
2
3
4
5
6
7
8
9
10
c
d

FIG.2

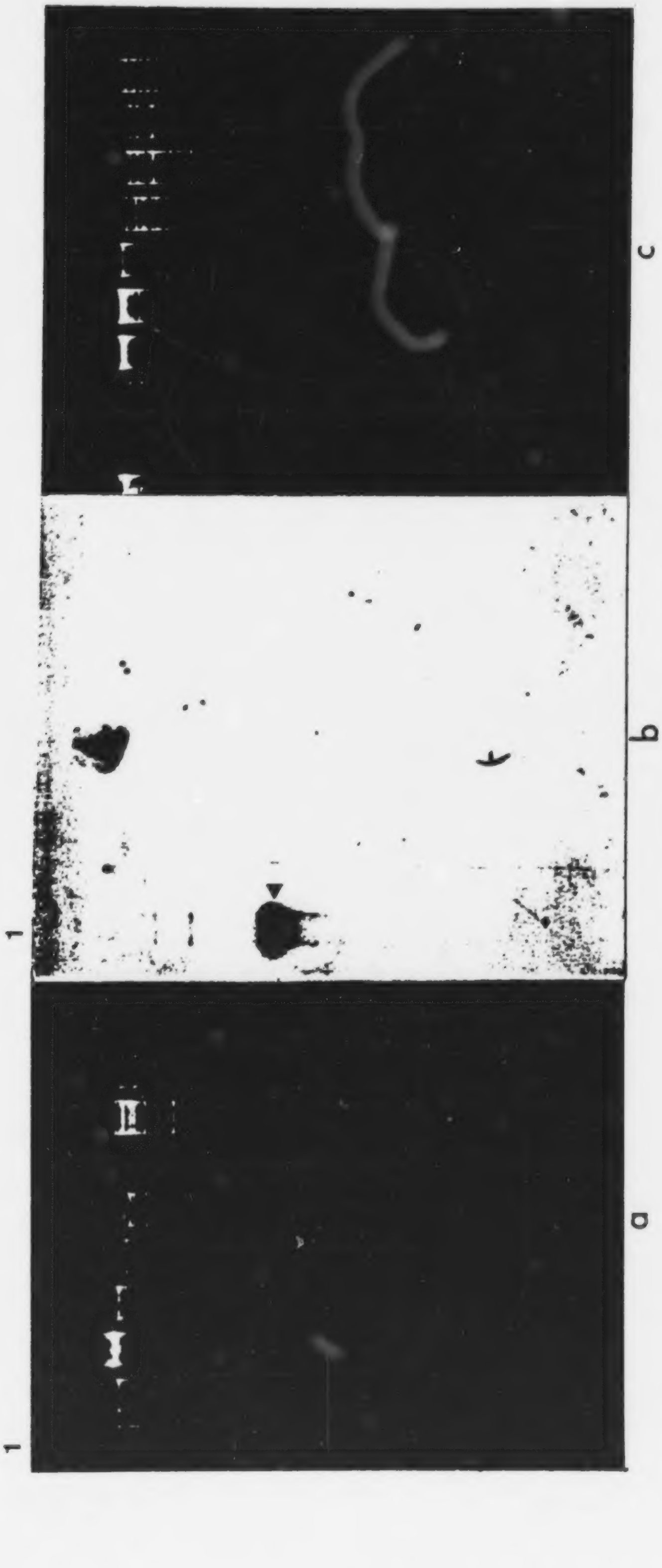

FIG.3

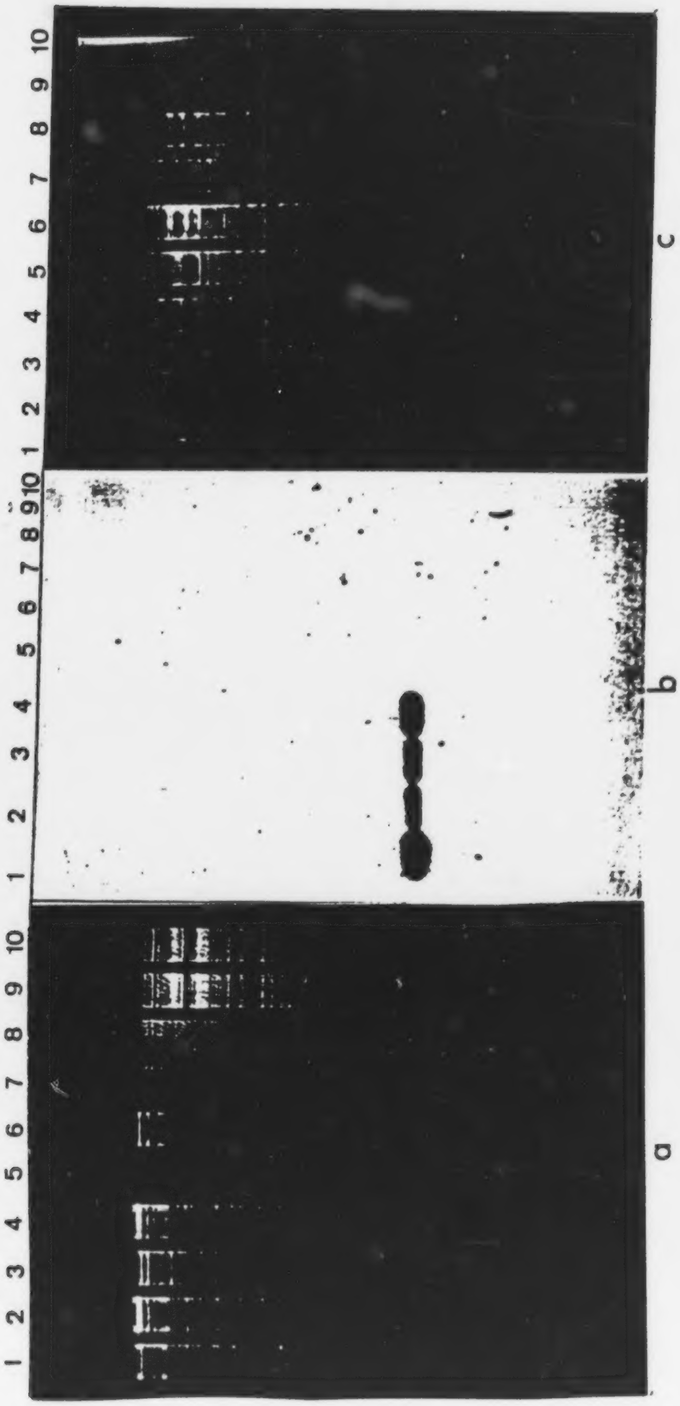
1 2 3 4 5 6 7 8 9 10
a
1 2 3 4 5 6 7 8 9 10
b
1 2 3 4 5 6 7 8 9 10
c

FIG.4

Table I

Biochemical identity and restriction endonuclease (REA) families of human source *Streptococci* and their reactions with goose probe #807 and human probe #1126.

		PROBE	
Identity	#807	#1126	REA Family
1. *S. durans* (Fig.4c,lane 1)		+	D
2. *S. durans* (Fig.4a,lane 1)	+		A
3. *S. durans* (Fig.4a,lane 7)			B
4. *S. durans* (Fig.4a,lane 2)	+		A
5. *S. durans* (Fig.4a,lane 3)	+		A
6. *S. durans* (Fig.4a,lane 4)	+		A
7. *S. durans* (Fig.4a,lane 8)			B
8. *S. faecium* (Fig.4a,lane 9)			C
9. *S. faecium* (Fig.4a,lane 10)			C
10. *S. faecium* (Fig.4c,lane 5)			E
11. *S. faecium* (Fig.4c,lane 6)			E
12. *S. faecium* (Fig.4c,lane 7)			
13. *S. faecium* (Fig.4c,lane 8)			
14. *S. faecalis var. liquefaciens* (Fig.4c,lane 2)		+	D
15. *S. faecalis var. liquefaciens* (Fig.4c,lane 3)		+	D
16. *S. durans* (Fig.4a,lane 5)	+		A
17. *S. faecalis var. liquefaciens* (Fig.4c,lane 4)		+	D
18. *S. faecalis var. liquefaciens* (Fig.4c,lane 9)			
19. *S. faecalis var. liquefaciens* (Fig.4c,lane 10)			
20. *S. faecalis var. liquefaciens* (Fig.4a,lane 6)	+		A

Table 2

Biochemical identity and restriction endonuclease (REA) families of gull source *Streptococci* and their reactions with goose probe #807 and human probe #1126.

Identity	PROBE #807	 #1126	REA Family
1. *S. faecalis var. liquefaciens*	+		A
2. *S. faecalis var. casseliflavis*			F
3. *S. faecalis var. casseliflavis*			
4. *S. faecalis var. liquefaciens*			F
5. *S. faecalis var. liquefaciens*			
6. *S. faecalis var. liquefaciens*			
7. *S. faecalis var. zymogens*			
8. *S. faecalis var. liquefaciens*			
9. *S. faecalis var. faecalis*			
10. *S. faecium*			
11. *S. faecalis var. zymogens*			
12. *S. durans*			
13. *S. faecalis var. liquefaciens*			
14. *S. faecalis var. zymogens*			
15. *S. bovis*			
16. *S. bovis*			
17. *S. faecium*			
18. *S. faecium*			G
19. *S. faecium*			G
20. *S. faecalis var liquefaciens*			

NOTE:

FOR STRAINS 1-10 SEE FIGURE 3A, LANES 1-10; FOR STRAINS 11-20 SEE FIGURE 3C, LANES 1-10.

Plant Bioassays for the Detection of Environmental Mutagens

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ABSTRACT

It is well established that higher plants provide valuable assay systems for screening and monitoring environmental chemicals (de Serres 1978; Grant 1978, Grant *et al*. 1981; Nilan 1978). This project "Plant Bioassays for the Detection of Chemical Mutagens" was initiated in order to have a different relatively inexpensive mutagen assay system (using higher plants) which would provide a measurement of mutagenic toxicity in assay systems not being carried out by the Ontario Ministry of the Environment. This study involves the use of two higher plants, namely, *Tradescantia* and Barley (*Hordeum vulgare*). The *Tradescantia* assay systems are: (1) the Stamen Hair Assay for the detection of gene mutations, and (2) the Micronucleus Test for the detection chromosomal aberrations. The assay system to reported in barley is the Root Tip Chromosomal Aberration Assay. Ethyl methanesulfonate (EMS) is being used as a positive control. Tests are being completed on three herbicides, namely, alachlor (Lasso), atrazine, and metolachlor. Preliminary results indicate all three herbicdes give a postive response in these plant assays. The herbicide atrazine is strongly mutagenic. The number of mutations from a dose of 50 ppm exceeded the number produced by a 250 ppm dose of EMS used as a positive control. Metolachlor also is mutagenic with the number of mutagenic events from a 240 ppm treatment exceeding the equivalent of 250 ppm EMS. In the stamen hair assay, the mutagenicity of Lasso was not significantly different from the control, however, Lasso caused a high percentage of chromosome aberrations in the micronucleus assay which was double those resulting from a 500 EMS treatment. Lasso also induced fragments in the barley chromosome aberration assay. From the chromosomal data, Lasso is considered to be a strong clastogen. The results to date indicate that higher plant assays are highly suitable for testing for the mutagenicity of environmental chemicals from air, soil and water habitats.

Introduction

Higher plants provide valuable assay systems for screening and monitoring environmental chemicals, both gaseous and liquid (Grant *et* al. 1981). Although higher plant assays for the detection of mutagens have been in existence for many years, they have only recently received the recognition which these sensitive and reliable systems warrant (de Serres 1978; Grant 1978; Nilan 1978). As Stich and San (1980) stated "The recent successful introduction of the use of Tradescantia staminal hairs to detect airborne mutagens and carcinogens, may be the beginning of the recognition of various plant assays which are inexpensive, easy to handle and applicable to indoor as well as outdoor detection of environmental mutagens". Studies have shown that, for a specific chemical agent, comparable results in terms of genetic abnormalities are obtained in plant and animal systems. For example, in a survey of studies on the effects of pesticides, it has been shown that an excellent correlation exists between the frequency of both chromosomal abnormalities and C-mitoses in plant and animal systems (Grant 1978). A similar conclusion was drawn in studies on the effect of eight chemicals in several systems, including in vitro and in vivo mammalian systems, bacteria, Drosophila and plant systems. The plant systems showed excellent correlations with the mammalian systems (Clive and Spector 1978).

This project using higher plant assays was initiated in order to complement information provided by other mutagen assay systems being carried out by the Ontario Ministry of the Environment. In this study, two higher plant systems are being used:

(1) Tradescantia clone 4430, heterozygous for flower color, blue dominant to pink recessive, developed at the Brookhaven National

Laboratory originally for the study of the effects of irradiation (Underbrink et al. 1973)

Assays: (a) The staminal hair assay system will detect
air borne, soil, and aqueous mutants
(Ichikawa, S. 1978; Schairer et al. 1978)
(b) The micronucleus assay will detect
chromosome aberrations (Ma 1981).

(2) Hordeum vulgare (barley):

Assay: Root tips for the detection of mitotic
chromosome aberrations (Wuu and Grant 1966).

Protocols

Protocols have been fully developed for both the Tradescantia and Barley assays. A brief outline of these assays is given below and in greater detail in Tables I, II, and III.

Tradescantia

Tradescantia plants propagate readily, and initial emphasis was placed on the use this plant as a test organism as it is highly sensitive to chemical mutagens.

For the Stamen Hair Assay, inflorescences of the appropriate age are placed in a drop of paraffin oil and observed under a dissecting microscope. Pink mutant cells are scored. Details of the protocol are given in Table I.

For the Micronucleus Assay, pollen mother cells which are highly synchronized in Tradescantia are examined in the quartet (tetrad) stage (about 24 hours prior to anthesis) and micronuclei are scored. The micronuclei reflect chromosome aberrations which occurred at earlier stages in meiosis. The frequency of micronuclei per 100 cells can be used as an index of mutation. Details of the Protocol are given in Table II.

Barley

Barley seed is germinated in petri dishes in an incubator at 22 C. Seeds are treated and root tips of young seedlings are examined for chromosome aberrations. The protocol for the Barley Chromosome Aberration Assay is given in Table III.

Results to date

Tradescantia

Ethyl methanesulfonate (EMS)

A number of tests have been carried out using EMS as a positive control, since this chemical has been shown previously to give a positive response in both the Tradescantia Stamen Hair (ST) and Micronucleus (MCN) assays.

The results of several experiments are given as examples of our EMS studies which were carried out to validate the assay systems.

Stamen Hair Mutation Assay

In general, the mutation rate in stamen hairs with EMS is well above control values (Fig. 1). Tables IV is a representative experiment with 500, 1000, and 1500 ppm. Fig. 1 illustrates the results given in Table IV, and Fig. 2 the results of the EMS treatment minus the control. As may be seen (Fig. 2), there is only a slight increase in the mutation rate at the 1500 ppm concentration over the 1000 ppm. It may be that 1500 ppm is approaching the onset of toxicity.

Tradescantia Micronucleus (MCN) Assay and EMS Treatments

Tables V presents data on 25 and 100 ppm EMS treatments. As may be seen from this table, there is a strong positive response with EMS in the MCN test.

Results with Pesticides (Herbicides)

Atrazine

Representative results for treatments with the herbicide atrazine in the Tradescantia Stamen Hair assay are shown in Table VI and in Fig. 4. EMS at a concentration of 250 ppm is included as a positive control. The 50 ppm treatment gave almost double the number of mutations of the 250 EMS control (Table VI). The 25 and 50 ppm treatments gave a positive dose response, but the 100 ppm treatment, although above the control value, indicated that this concentration was approaching the toxic limit.

Alachlor (Lasso)

Representative results of treatment with Lasso in the stamen hair assay are given in Table VII and Fig. 5, along with a 250 ppm EMS treatment as a positive control. Results for the Micronculeus Test are given in Table VIII and in Fig. 6. As may be seen in Table VII, the results of all treatments were above both the water control and the EMS positive control. All treatments gave over double the number of mutations observed for the control. From the data presented, it may be seen that Alachlor induces both gene mutations and chromosome aberrations.

Metolachlor

Representative results for treatments with the herbicide metolachlor for the Micronucleus assay are given in Table IX. In Table IX, results of 240, 480 and 960 ppm treatments are given along with 500 ppm EMS as a positive control. As may be seen from this table and Fig. 7, only the 960 ppm treatment is strongly positive (over double the control). The 240 and 480 ppm treatments do not differ significantly from the control.

Barley

Some representative results of chromosome aberrations using barley as the test organism are given in Tables X and XI. As expected, a positive dose response was obtained for chromosome aberrations with EMS (Table

X). Chromosome aberrations included: stickiness, breaks, bridges, lagging chromosomes and polyploid cells.

Alachlor (Lasso): From the data (Table XI), it may be seen that Lasso causes chromosome aberrations and induces chromosome fragmentation (500 ppm for 3 and 6 hours treatments). The concentration of 1500 ppm for 24 hours was toxic and inhibited cell division.

Conclusion on the Mutagenic Effect of the Herbicides Tested

Atrazine

From the data presented it may be seen that Atrazine causes gene mutations. A 50 ppm treatment gave over three times the number of mutations as the control (Table VI). Atrazine has previously been shown to induce reverse mutations in the waxy locus of corn (Plewa and Wagner 1981). Atrazine has been reported to cause chromosome aberrations in plants (Wuu and Grant 1966, 1967).

The true mutagenic effect of atrazine may not be the result of treatment with atrazine *per se*, but a metabolic product which is produced in plants and which causes its mutagenic/chromosome aberration effects (Gentile *et al*. 1978; Plewa 1978).

Alachlor (Lasso)

Lasso caused both gene mutations (Table VII) and chromosome aberrations in Tradescantia (Tables VII, VIII) and in barley (Table XI). Lasso has been reported to cause reverse mutations in the waxy locus in corn (Plewa and Wagner 1981) and chromosome aberrations in barley (Singh et al. 1978).

Metolachlor

Metolachlor was only slightly positive in the production of mutations in the stamen hair assay, but was quite positive for the production of chromosome aberrations in the micronucleus test (Table IX).

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TABLE I. Protocol for the *Tradescantia* Stamen Hair (ST) Assay

The *Tradescantia* Stamen Hair Assay was developed by A. H. Sparrow of Brookhaven National Laboratory for the study of the effects of ionizing radiation. Early radiobiological data demonstrated that stamen hairs were sensitive to as little as 0.25 rad of x-rays. Stich and San (1980) have stated "The recent introduction of the use of *Tradescantia* staminal hairs to detect airborne mutagens and carcinogens may be the beginning of the recognition of various plant assays which are inexpensive, easy to handle and applicable to indoor as well as outdoor detection of environmental mutagens."

For environmental chemicals, the *Tradescantia* clone 4430 has been developed at the Brookhaven National Laboratory. This clone is heterozygous for flower color and staminal hairs. Mutations are detected by the change in color from blue to pink.

The Staminal Hair Bioassy involves:

a) Making cuttings of young inflorescences prior to meiosis. Grow cuttings in aerated Hoagland's nutrient solution.

b) Expose the young inflorescences by placing the cuttings in the test chemical and allowing the liquid to absorb through the stem to the inflorescence. One flower will develop about 400 stamen hairs.

c) Collect flowers daily from 8 to 20 days after treatment (if chemical causes severe toxic effect flower development may be delayed, then examine as long as 25-30 days after treatment). Put flowers in a container with moistened sponge in refrigerator until ready to examine.

d) Prepare slides by placing a stamen in liquid parafin for microscopic examination; add cover slip. Examine immediately if possible, or place in refrigerator for same day examination.

e) Cytological Examination: Examined at a magnification of 400X (10 X ocular and a 40 X objective). Use white light source (no filters) for the detection of pink mutations.

f) Statistics: Examine and score as in the following example: Score 18 stamens per treatment per day from 18 different cuttings. Score daily as above. Mutations are recorded as pink events per 100 or 300 stamens.

A complete description of the technique with illustrations are given in the paper by Schairer et al. (1978) and Underbrink et al. (1973). References are given at the end of the report.

TABLE II. Protocol for the Tradescantia Micronucleus (MCN) Bioassy

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The meiotic pollen mother cells (PMC) of _Tradescantia_ are highly synchronized and are very sensitive to physical and chemical mutagens (Ma, 1981). A high frequency of acentric fragments can be induced with very low level of mutagens. These induced chromosome aberration become micronuclei (MCN) in the synchronized tetrads and they can be easily identified and scored.

The MCN Bioassy involves:

a) Making cuttings of young inflorescences prior to meiosis. Grow cuttings in aerated Hoagland's nutrient solution.

b) Exposure of PMC in the young inflorescence of the plants by placing the cuttings in the test chemical and allowing the liquid to absorb through the stem to the inflorescence just prior to the onset of meiosis.

c) Fix flower buds 9 to 12 days after exposure (testing one or two buds prior to fixation to confirm that meiosis has proceeded to the tetrad stage) in acetic-alcohol (1:3).

d) Prepare microslides by removing a few PMc's at a time and squashing the cells in aceto-carmine stain. The stain penetrates fairly readily, but flaming over an alcholol lamp briefly will speed the staining process.

e) Cytological Examination: The tetrads are examined at a magnification of 400X (10 X ocular and a 40 X objective).

f) Statistics: An examination of 300 tetrads per slide and five slides per treatment have been found to give highly significant results.

A complete description of the technique with illustrations are given in the paper by Ma (1981). Earlier references are given in Ma's paper. Reference is given at the end of the report.

Table III. Protocol for the Barley Chromosome Aberration Assay

1a. Barley seeds, 50 seeds per petri plate are prepared and treated* without presoaking.
1a. Tradescantia cuttings are made and placed in beakers. Beakers containing the treatment solutions are aerated with an air pump (aquarium pump). During treatment, the beakers are covered with aluminum foil and sealed with parafilm.
2. Treatment
3. Washing
4. Recovery, 24 hours at 20 C.
5. Harvest roots
6. Pretreatment: 0.003 M 8-hydroxyquinoline, 1-3 hours
7. Fixation, Carnoy's (3:1, 95% ethanol-glacial acetic acid), at 0-4 C for 12-24 hours (16 h)
8. Hydrolysis, 1N HCl at 60 C for 10 min for root tips and 20 min for flower buds
9. Stain, basic fuchsin for 1 hour at 30 C in the dark.
10. Destaining, 3 changes of SO2 water for 15 min each.
11. Storage, 70% ethanol in a refrigerator
12. Preparation: Rinse in water, 3 changes
13. Maceration: 4% pectinase, 1 to 3 hours
14 Slide preparation: Squash in 45% acetic acid
15a. Temporary slide: seal with rubber cement
15b. Permanent slide: Slide is placed on dry ice; remove cover slip with razor blade; root tip material adheres to slide; immerse in 2 changes of absolute alcohol and mount in Euparol, Permount or equivalent.

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*For those chemicals which are not water soluble, the chemical is dissolved in dimethyl sulfoxide (DMSO). Treatments are applied for a period of 6 to 24 hours with a 24 hour recovery period.

Table IV. Tradescantia Stamen Hair Mutation Assay, 6 hour treatment with ethyl methanesulfonate (EMS)
Prepared 291085

Dosage (ppm)	No. flowers scored	No. of hairs	Number of Pink events	Mutations	Scoring
				No. /100 hairs	period
0	43	16,770	96	0.57 + 0.29	141085-291185
500	46	16,560	183	1.10 + 0.46	111085-281185
1000	30	10,620	148	1.39 + 0.78	121185-281185
1500	32	12,288	175	1.42 + 0.89	111185-271185

Table V. Tradescantia Micronucleus (MCN) Mutation Assay, 6 hour treatment with ethyl methanesulfonate (EMS), 2.5 days recovery.
Prepared: 050386.

Dosage (ppm)	Number of MCN/300 Tetrads	Number of Tetrads scored	Mean number of MCN/300 Tetrads	Number of cells with MCN/300 tetrads	Mean no. cells with MCN/300 tetrads
0	20	2,297	2.5 + 1.7	15	1.88 + 1.2
25	121	2,400	15.1 + 5.6	116	14.50 + 5.1
100	270	2,993	27.0 + 9.6	234	23.40 + 3.2

Table VI. Tradescantia Stamen Hair Mutation Assay, 6 hour treatment with ATRAZINE and 250 ppm ethyl methanesulfonate (EMS) as positive control. Prepared: 060586

Dosage (ppm)	No. flowers scored	No. of hairs	Number of Pink events	Mutations No. /100 hairs	Scoring period
0	28	8,568	70	0.82 + 0.10	120586-290586
250 EMS	34	9,588	192	2.00 + 0.93	140586-290586
25	43	12,384	171	1.38 + 0.57	190586-290586
50	44	13,728	483	3.52 + 1.48	150586-290586
100	22	6,072	75	1.24 + 1.12	120586-290586

Table VII. Tradescantia Stamen Hair Mutation Assay, 6 hour treatment with ALACHLOR (LASSO); 250 ppm ethyl methanesulfonate (EMS) used as positive control. Prepared: 120586.

Dosage (ppm)	No. flowers scored	No. of hairs	Number of Pink events	Mutations No. /100 hairs	Scoring period
0	16	4,992	49	0.98 + 0.47	210586-050686
250 EMS	22	5,808	115	1.98 + 1.12	220586-050686
300	37	11,100	230	2.07 + 0.77	220586-050686
500	33	9.504	259	2.72 + 1.37	210586-050686
700	24	8,064	202	2.50 + 1.32	260586-050686

Table VIII. Tradescantia Micronucleus (MCN) Mutation Assay, 6 hour treatment with ALACHLOR (LASSO); 500 ppm ethyl methanesulfonate (EMS) used as positive control. Prepared: 041085.

Dosage (ppm)	Number of MCN/300 Tetrads	Number of Tetrads scored	Mean number of MCN/300 Tetrads
0	41	4,565	2.73 + 0.64
500 EMS	53	4,799	3.31 + 0.55
125	102	4,175	7.28 + 2.44
250	70	3,570	5.83 + 1.81
500	51	3,769	4.25 + 1.00
1000	78	3,900	6.00 + 1.86

Table IX. Tradescantia Micronucleus (MCN) Mutation Assay, 6 hour treatment with METOLACHLOR; 500 ppm ethyl methanesulfonate (EMS) used as positive control.
Prepared: 020586.

Dosage (ppm)	Number of MCN/300 Tetrads	Number of Tetrads scored	Mean number of MCN/300 Tetrads
0	1.0	3,600	0
500 EMS	26	3,781	2.00 + 0.57
240	21	3,300	1.91 + 0.81
480	18	4,200	1.29 + 0.83
960	45	2,941	4.50 + 2.68

Table X. Barley chromosome aberration assay. Treatment with the positive mutagen, ethyl methanesulfonate (EMS)

Dosage (ppm)	Time (h)	No. dividing cells	Total no. cells	Mitotic index* $x 10^{-3}$	Total aberrations	Types
0	3	18	3555	5.06	0	
500	3	15	4835	3.1	3	Lagging chromosomes, clumping, spindles
500	3	40	1648	2.43	19	Breaks, laggards, fragments; polyploidy
1000	3	10	3789	0.264	1	Clumping
1000	3	6	3084	1.95	5	Stickiness, laggards fragments, micronuclei
1500	3	39	3258	1.20	4	Bridges, laggards, clumping
0	6	24	3400	7.59	0	
500	6	29	3804	7.62	3	Clumping
500	6	15	2784	5.39	5	Bridges, stickiness, laggards
1000	6	10	5440	1.84	4	Stickiness, polyploidy
0	24	188	6630	28.4	0	
500	24	21	2632	7.98	3	Chromosome breaks, polyploidy
1000	24	23	6720	3.42	4	Stickiness, clumping
1000	24	54	3584	1.51	7	Fragments, spindle, polyploidy
1500	24	44	1792	2.46	2	Telophase bridges

*Mitotic Index: indicates the fraction of the total number of cells scored in any stage of mitosis.

Table XI. Barley chromosome aberration assay; treatment with ALACHLOR (Lasso)

Dosage (ppm)	Time (h)	No. dividing cells	Total no. cells	Mitotic index x 10^{-3}	Total aberrations	Types
0	3	121	15708	7.70	1	Fragment
0	6	19	2634	7.21	0	
0	24	17	2870	5.92	0	
500	3	10	1760	5.68	4	Fragments
500	6	11	4149	2.65	2	Fragments
1000	3	20	1634	1.22	4	Fragments; stickiness
1500	3	16	1888	8.47	2	Fragments
1500	6	8	1649	4.85	0	Toxic, cells killed
1500	24	0	5196	0.00	0	Toxic, cells killed

Fig. 1.

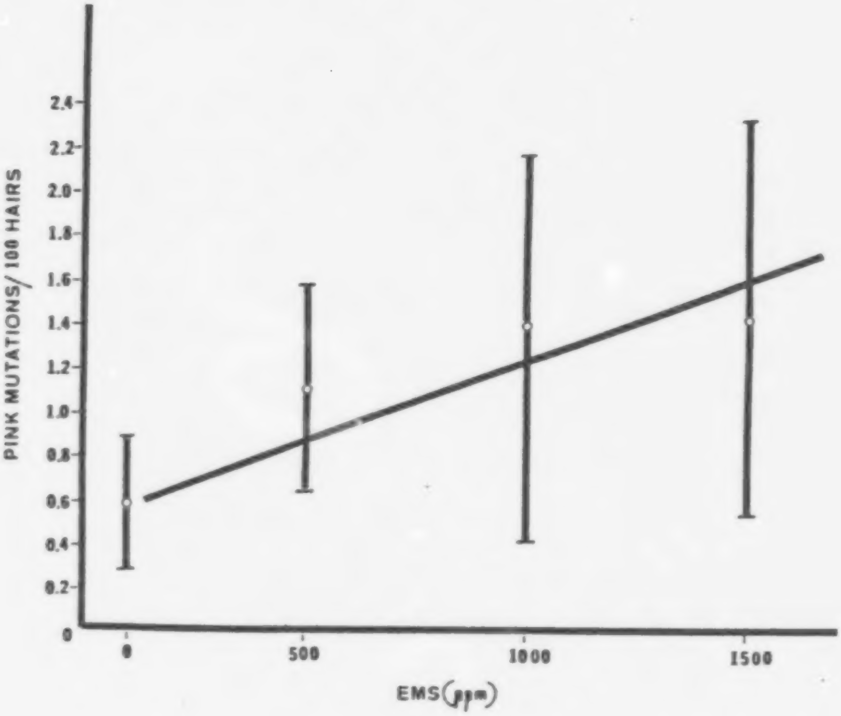
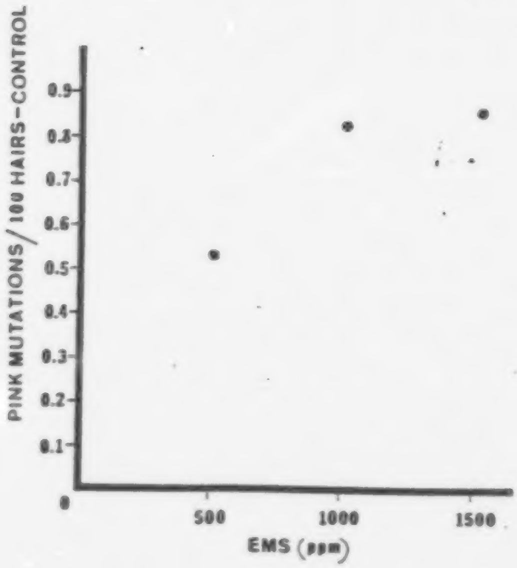

2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
PINK MUTATIONS/ 100 HAIRS
0
500
1000
1500
EMS(ppm)

Fig. 2.


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
PINK MUTATIONS/100 HAIRS-CONTROL
500
1000
1500
EMS (ppm)

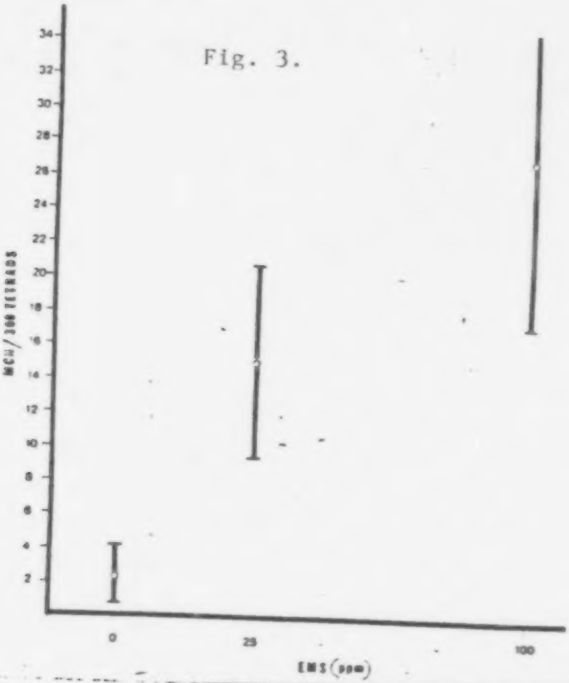


Fig. 3.

MCW/300 TETRADS
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
25
100
EMS (ppm)

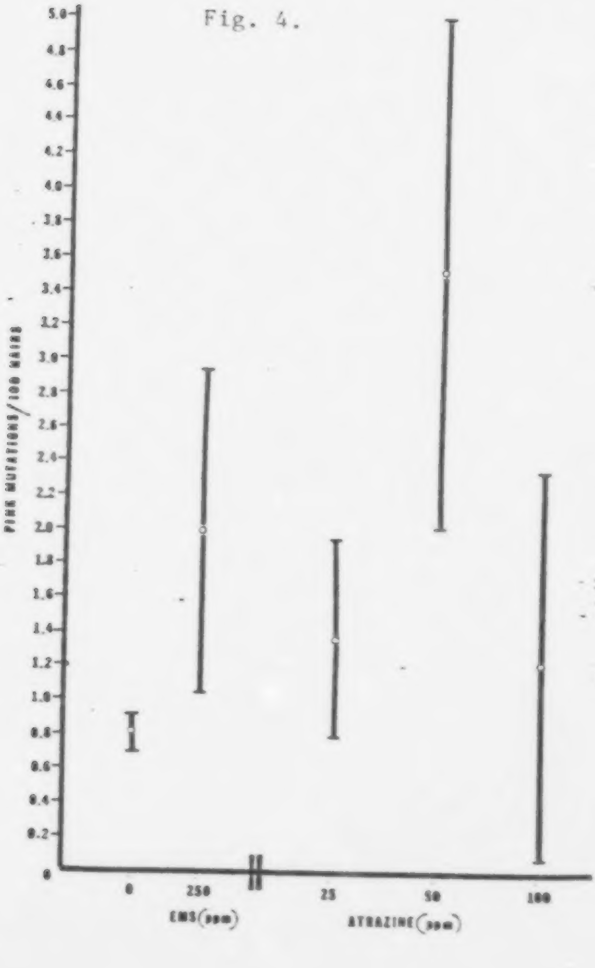


Fig. 4.

PINK MUTATIONS/100 HAIRS
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
250
25
50
100
EMS (ppm)
ATRAZINE (ppm)

Fig. 6.

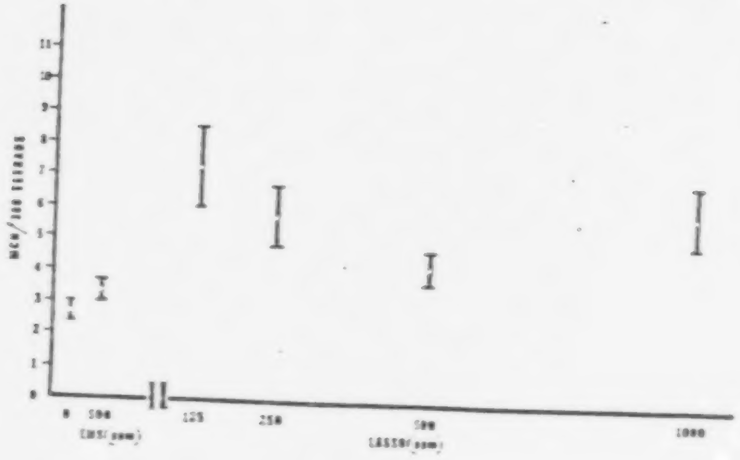


Fig. 7.

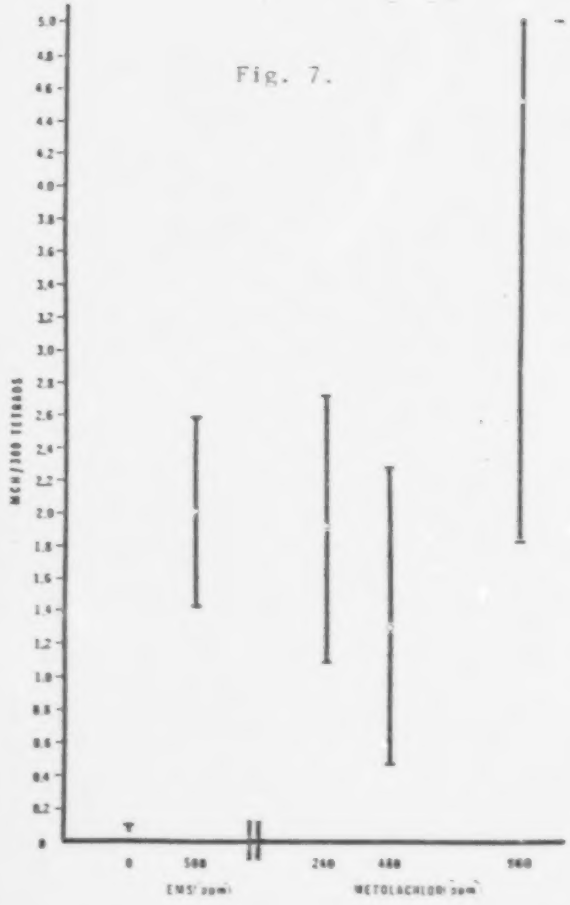
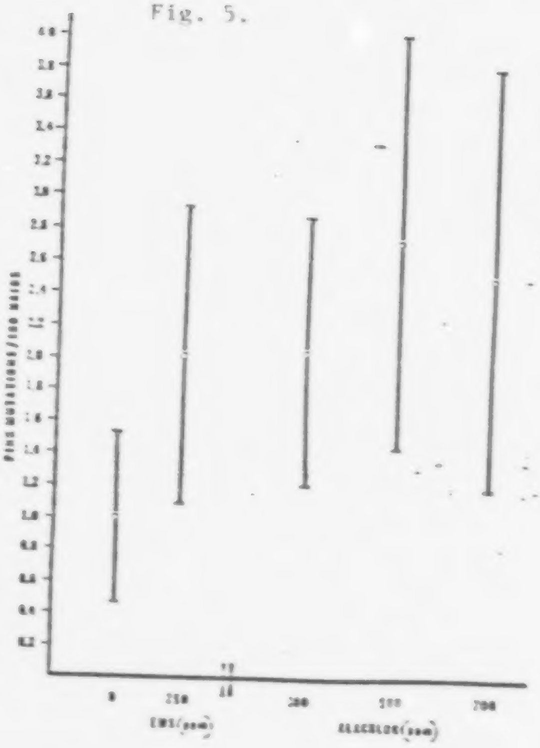


Fig. 5.



A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS

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INTRODUCTION AND BACKGROUND

In recent years, the occurrence of hyperplasia and neoplasia in fishes from the Great Lakes and other waters has received widespread attention as a possible indicator of water quality problems (see reviews by Baumann 1984 and Black 1984). There is circumstantial evidence that morphological abnormalities may also develop in benthos in response to sediment contamination. Most studies on abnormalities in freshwater macroinvertebrates have examined the occurrence of deformities in Chironomidae.

Brinkhurst et al. (1968) and Hamilton and Saether (1971) reported that specimens of Chironomus spp. collected from the western end of Lake Erie near the Maumee River mouth were badly deformed. The most conspicuous feature of these larvae was an exceedingly thick exoskeleton. The head capsules were also thickened and heavily pigmented, and the mouth parts exhibited a variety of aberrations. Stations from the remainder of the lake yielded more than 1,700 specimens, all of which appeared normal.

Warwick (1980a) recovered remains of deformed chironomid larvae, with deformities similar to those described by Brinkhurst et al. (1968), from sediment cores collected in the Bay of Quinte, Lake Ontario. The percentage of deformed specimens of Chironomus and Procladius clearly increased in the most recent sediments. According to the sediment core chronology, the incidence of deformities increased from 0.09% in the pre-European sediments to 1.06% at 4.5 cm (1951) and 1.99% in the 1972 chironomid population.

In a study of the benthic community in Parry Sound, Georgian Bay, Hare and Carter (1976) found that 77% of Chironomus (s.s.)? cucini larvae had deformities of the mouthparts. Refuse entering Parry Sound Harbour during the past 100 years from lumbering, smelting and explosives industries, as well as urban sewage, has left the sediments visibly contaminated with oil, cinders and saw-mill leavings. The harbour was the site of a massive oil spill in 1950. Of 73 larvae examined from outside the harbour only one specimen was found to be slightly deformed.

Cook and Veal (1968) reported that most of the chironomids (Chironomus spp.) at a sampling station in the turning basin of Port Hope Harbour, near the cooling water discharge of a uranium refining plant, had deformed labial plates similar to those described by Brinkhurst et al. (1968). McKee et al. (1985) and Warwick et al. (1986) reported a deformity frequency of 83% for Chironomus specimens collected in the turning basin compared with only 14% in the outer harbour. Sediment quality data showed that the inner harbour is heavily contaminated by U-238 decay chain radionuclides and several trace metals, particularly in the turning basin, while the outer harbour is relatively uncontaminated.

Several other investigators also have reported deformities in Great Lakes chironomids. Boscor et al. (1974) reported increased frequencies of deformed Chironomus in Black River Bay, Lake Ontario, and implicated pollution by agricultural and industrial toxicants as a probable causal factor. Crowther and Luoma (1984) reported the occurrence of deformed larvae of C. salinarius in a habitat impaired by pulp and paper mill discharges in Thunder Bay, Lake Superior. In a survey of benthic macroinvertebrates of the central basin of Lake Erie, Krieger (1984) reported that one specimen of Chironomus near the mouth of the Grand River at Fairport Harbor and two specimens of Procladius near the mouths of the Black River at Lorain and the Cuyahoga River at Cleveland possessed deformed menta or ligulae, respectively. The occurrence of deformed chironomids in polluted waters outside of the Great Lakes basin has been reported by Nelson and Blaylock (1963), Blaylock (1965), Hamilton and Saether (1971), Koehn and Frank (1980), Warwick (1980b), Tennessen and Gottfried (1983), Cushman (1984) and Wiederholm (1984).

These studies on the occurrence of deformed chironomids in areas affected by industrial and/or agricultural pollution suggest the hypothesis that sediment contamination may induce chironomid deformities, and the possibility that deformity frequency may be used as a sediment quality indicator. However, a number of questions remain to be answered. In particular:

1. Can deformities similar to those seen in the field be induced by life-cycle exposure of normal stock to known genetic toxicants?
2. To what extent do observed deformities have a heritable genetic basis?
3. Can deformities be induced by physical (e.g., grain size, temperature) as opposed to chemical factors?

These questions are fundamental to our understanding of a chironomid indicator system and what it may tell us about sediment quality, and are best addressed in controlled laboratory experiments.

The only previous laboratory experiments in which any of these questions have been addressed are those of Hamilton and Saether (1971). These authors exposed cultures of Chironomus tentans through one life cycle (egg to 4th instar) to lethal concentrations of aldrin, DDE, PCB's and 1:1 2,4-D:2,4,5-T. A small proportion (≃10%) of the larvae surviving exposure to 10 ug/L of DDE in solution were found to be deformed with thickened body walls. Deformed mouthparts were not observed.

Cushman (1984) indicated that laboratory studies were necessary to establish causal relationships between deformities and particular toxicants, e.g., with larvae from single egg clusters reared at different dose levels, so that the exposure histories of the larvae and their parents are known. The laboratory studies described in this report were designed to determine whether mouthpart deformities could be induced in chironomids by a known genotoxicant, ethyl methane sulfonate (EMS), either in exposed organisms or in their unexposed offspring.

METHODS

Culture Conditions

A stock culture of Chironomus tentans was established from ten egg masses collected in the field by B.E. Townsend, Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Manitoba. The stock culture was maintained in the laboratory for three generations prior to initiating experiments on deformity induction. Culture methods follow Townsend et al. (1981) and Batac-Catalan and White (1982). Air temperature was maintained at $25^{\circ} \pm 2^{\circ}C$ and photoperiod at 16L:8D.

The culture was reared in a 40-L glass aquarium with 5 cm of fine sand on the bottom. The aquarium was supplied with carbon-filtered tap water at a rate of 0.5l/hr and a water level of 10 cm was maintained by a standpipe drainage system. The water volume was 15L. Aeration was provided by a single airstone. The culture was fed ad libitum with a slurry of either Cerophyl, a dried plant product, or Tetramin fish food, every three days. The amount increased with the stage of development and food requirements of the culture, and was sufficient to prevent the formation of food-clear areas around the developing larvae. Excess food and debris were gently siphoned from the bottom before each feeding.

The aquarium was covered with a fine mesh screen in order to prevent the escape of emerging adults. Adults were collected from the aquarium by aspiration into an Erlenmyer flask containing fresh water to a depth of 3 cm. They were confined to the flask by a cotton wool stopper, in a sex ratio of 2 males to 10 females, and left overnight to mate. Egg masses collected the following morning were used to start a new stock culture with clean sand and water.

Experiments were conducted under conditions similar to those used for stock culture maintenance, except that each egg mass was reared in a separate 1-L culture bowl with its own air supply. Water or test solution was siphoned out of the bowl, almost to substrate level, and replaced prior to feeding every three days. Tetramin was used as a food source during preliminary toxicity experiments, while Cerophyl was used in subsequent experiments on deformity induction. Tetramin was prone to fungal growth under semi-static culture conditions.

EMS Toxicity Determinations

Preliminary toxicity experiments were conducted in order to estimate the LC50 concentrations of EMS and establish a sublethal dose range for future experiments on deformity induction. Replicate test cultures were established at EMS concentrations of 0, 50, 100, 500, 1,000 and 5,000 mg/L. Exposure was initiated on the day following egg mass deposition and continued through the 4th instar stage. The 4th instar larva is 12-24 mm in length, bright red in colour, and distinguished from previous instars by a dark dorsal head stripe.

The number of eggs in each egg mass was counted under a dissecting microscope prior to placement of the egg mass in the test solution. The culture was decanted and preserved in 10% formalin when the first pupae were observed, and then washed through a 500 um mesh screen. Larvae and pupae were counted, and divided by the initial egg count to give a survival estimate.

The approximate LC50 concentration of EMS was estimated as the midpoint between two adjacent exposure levels, marked by apparently normal survival at the lower level (100 mg/L) and complete mortality at the next higher level (500 mg/L). Confidence limits could not be determined due to the lack of a graded response series at intermediate exposure levels.

Determination of Sublethal Effects

Experiments on deformity induction were conducted at exposure levels of 0, 50, 75, 100 and 240 mg/L, with two replicate cultures at each concentration. Exposures spanned the period from egg mass deposition through 4th instar, as previously described. However, some larvae from each culture were allowed to complete pupation and emerge as adults. Culture bowls were covered with a fine screen mesh to prevent adults from escaping. Emerging males were collected each day for several days and mated with virgin females from the control cultures, in order to determine from their offspring whether heritable genetic damage had been induced. Then both exposed and control cultures were preserved as previously described.

Virgin females were isolated by placing individual pupae just prior to emergence in individual glass jars containing clean water and covered with a fine mesh screen. Some of the adults emerging in these jars were males and were discarded. Others were females and were paired with individual males from exposed cultures in Erlenmyer mating flasks. Each egg mass deposited was counted and placed in a separate 1-L culture bowl, labelled according to the exposure history of the parents. These cultures were reared through 4th instar without exposure to EMS, and then preserved.

Preserved organisms from each culture, whether they had been directly exposed, derived from exposed male parents, or controls, were washed, sorted and counted as previously described. Counts of larvae, pupae and adults were divided by initial egg counts to estimate culture survival. Fourth instar larvae were blotted on tissue paper and weighed en masse to determine average weight for each culture. One hundred 4th instar larvae from each culture, or the total number if less than 100, were cleared and mounted for microscopic examination of their mouthparts.

Clearing and mounting techniques followed Warwick and Casey (1982), except that only the head capsules were mounted. Head capsules were severed from the body after clearing in cedar oil and prior to mounting in Canada Balsam. The bodies from each culture were stored in 70% ethyl alcohol.

Scoring of mouthpart deformities was conducted by double blind microscopic examination of the hypostomial plate, after each investigator had been 'trained' on the same series of sample slides designated normal or abnormal. Normal mouthpart anatomy is illustrated in Figure 1. Abnormalities included the following types:

1. missing or fused lateral teeth;
2. extra lateral teeth;
3. wide gaps between two teeth (the 'Koehn' gap);
4. missing or fused processes of the median tooth (normally trifid);
5. extra processes or dissection of the median tooth;
6. missing or fused processes of the first lateral tooth (normally bifid); and
7. extra processes of the first lateral tooth.

Typically, abnormalities were assymetrical, except in several control cultures. In one, a symetrical partial fusion of processes on both the right and left first lateral tooth was common while, in the other, a cleft median tooth was common. These symetrical characteristics were scored as abnormalities. Cases of obvious physical damage to the teeth, while rarely observed, were excluded from the abnormality count.

The abnormality frequencies determined by two investigators were averaged to compute a final abnormality score for each culture examined. Investigators agreed on 90% or more of the slides examined from each culture, except for a concordance of only 78% on the control with symmetrical partial fusion of processes on the first lateral.

RESULTS AND DISCUSSION

Chronic Embryo-Larval Toxicity

Preliminary experiments on embryo-larval toxicity of EMS were undertaken to establish a sublethal exposure range for later experiments on deformity induction. Preliminary exposures spanned two orders of magnitude from 50 mg/L to 5g/L. Survival from egg to 4th instar is shown in Table 1 for exposed and control cultures.

Low survival in control cultures (20 to 26%) may be related to loss of temperature control at one point prior to hatching when temperature fell overnight from 20°C to about 3°C. Townsend et al. (1981) report hatching failure at a temperature of 8°C throughout embryonic development, and Sadler (1935) reports developmental arrest in 4th instar at constant temperatures less than 8°C. Apparently normal hatching occurred in control cultures and those exposed to EMS at low levels.

Cultures at 100 mg/L and higher exposure levels were not followed beyond 4th instar in this experiment. However, adults were allowed to emerge and mate at 50 mg/L as a check on reproductive success.

At 100 mg/L EMS survival to 4th instar was apparently normal. At 500 mg/L EMS complete mortality occurred following hatching. Hatching was confirmed after disintegration of the egg mass, by microscopic examination of substrate samples, which contained large numbers of first instar larvae. No attempt was made to count these larvae and none survived to the visible 2nd instar stage.

At 1 g/L and higher levels of EMS hatching did not occur. Eggs turned white within the egg mass, which then failed to disintegrate normally. The culture was disposed of after 5 days, at which time no eggs with normal colouration were present.

On the basis of these experiments the LC50 for embryo-larval survival through 4th instar was estimated at approximately 300 mg/L EMS, although in the absence of intermediate exposure levels producing a partial mortality response, the actual LC50 may be anywhere in the range from 100 mg/L to 500 mg/L.

Survival through Emergence

A second series of embryo-larval exposures were conducted in the range from 75 mg/L to 400 mg/L EMS, in order to observe sublethal effects. Numbers of chironomids at each stage of development when cultures were preserved are shown in Table 2. One replicate at each exposure level was preserved when adults first began emerging; the other approximately one week later. Adults which emerged successfully are included in the table, even though they were not preserved with the culture. Adults which died while emerging or within hours of emerging are not included.

Control survival was better in these experiments (49-80%) than in the preliminary toxicity experiments, in spite of the later developmental end points used. Improved survival was probably due to the more stable thermal regime. The use of Cerophyl as opposed to Tetramin for feeding may also improve survival in semi-static culture.

Death at emergence was a common syndrome at 100 mg/L where most of the adults which began to emerge failed to complete the process. They seemed unable to detach themselves from the pupal case, an exercise which requires vigorous muscular action. Emerging adults were much less active in general at this exposure level than in control cultures. Dead midges attached to their pupal cases were also common at 75 mg/L.

Post-emergence mortality was the predominant adult mortality syndrome at 75 mg/L. Many adult midges would shed their pupal case, but drown before the daily collection from the culture. This also occurred in control cultures, but not with the same frequency since the majority of control adults were collected alive.

At 240 mg/L no adults emerged although many larvae pupated in apparently normal fashion.

At 400 mg/L only 10 larvae reached the 4th instar stage, out of 4200 eggs in two cultures. None of these larvae either formed tubes in the substrate or pupated. Numbers of survivors at this dose level were considered insufficient for determination of larval weight or deformity incidence.

Weight of 4th Instar Larvae

Average larval weight was determined in cultures exposed to EMS at concentrations between 50 mg/L and 240 mg/L. Larval weight was greatest in cultures exposed at 100 mg/L EMS, and lowest in the control cultures. Table 3 illustrates an increase in larval weight up to the 100 mg/L dose level, followed by a weight decline at

240 mg/L. The weight increase with dose level is probably the result of decreasing culture densities (Table 2) associated with reduced survival. The decline in weight at 240 mg/L may reflect toxic effects of EMS, or simply an additional manifestation of the density effect. Larval density was greater at 240 mg/L than at 100 mg/L, at least in part due to the greater numbers of eggs in the initial egg masses at 240 mg/L.

The normal average weight for late 4th instar larvae, according to Townsend _et al_. (1981), is 22 mg for male larvae and 37.7 mg for female larvae. Both male and female larvae contribute to the weights shown in Table 3. While the sex ratio was not determined, average weights between the normal male and female averages would be expected in the absence of crowding. This weight range was achieved only in 100 mg/L cultures, suggesting possible crowding effects in the other cultures. Crowding probably contributes to the wide range of developmental stages observed at the time of culture preservation.

Larval Deformities

The frequency of 4th instar larvae with abnormalities of the hypostomial plate was determined in cultures exposed to EMS at concentrations between 50 mg/L and 240 mg/L, and in control cultures. The 50 mg/L culture was established as part of the chronic toxicity experiment. Thus two sets of control cultures were scored for hypostomial deformities, one set concurrent with the 50 mg/L exposure, the other concurrent with exposures from 75 mg/L to 240 mg/L.

Deformity incidence is summarized in Table 4 for the exposed generation, and for the offspring of parents exposed at 50 mg/L. Both parents of this F_1 culture had been exposed to EMS. Thus it is not possible to rule out cytological effects of EMS on the developing ova of female parents, or to distinguish such cytological effects from genetic effects in the F_1 culture. The deformity incidence in this F_1 culture (33%) was greater than in any control culture, and greater than in the parental cultures at 50 mg/L, suggesting an EMS effect due to parental exposure. However, due to a fairly high and variable control incidence, and lack of replication of F_1 cultures, this result is not considered conclusive.

The effects of EMS on morphology of exposed larvae were more demonstrable. Deformity incidence was dose related and doubled relative to controls at 100 mg/L and 240 mg/L (Figure 2). The deformity incidence differed significantly from concurrent controls at 240 mg/L, based either on a student's t-test comparing mean deformity frequencies after angular transformation, or on chi-square tests comparing individual replicates ($p < 0.05$ in both cases).

The types of deformities observed are categorized in Table 5 for each culture. These data suggest a tendency to certain types of abnormalities in different cultures. This tendency was particularly evident among control cultures and may be related to the individual genetics of the parents producing each egg mass.

For example a predisposition toward cleft median teeth was seen in Control 1, where this specific condition accounted for 10 of the 19 hypostomial abnormalities observed. A predisposition toward partial fusion of the two processes of the first lateral tooth was seen in Control 2. The fusion was seldom complete, and was variable in degree. Arbitrarily, teeth showing an acute angle between the two processes were considered normal; those showing less separation were considered abnormal.

The conditions described above in Controls 1 and 2 were highly symetrical. The cleft in the median tooth usually divided it into two equal lobes, and similar degrees of fusion were observed in right and left first lateral teeth. While clearly abnormal, the symmetry of these conditions was consistant with an inherited genetic basis. Somatic damage is much less likely to be symmetrical.

Hare and Carter (1976) considered only asymmetrical defects of the mentum in estimating deformity incidence in chironomids from Perry Sound Harbour. We have included symmetrical defects in our estimates of deformity frequency. Symmetrical defects were rare in EMS-exposed cultures. However, their exclusion would approximately halve the deformity frequency reported for Controls 1 and 2 in Table 4.

The frequency of deformities observed in control cultures was higher than that typically reported for field collections of chironomids from pristine locations. Frequencies in such field collections have seldom exceeded 1%. As discussed above, high control frequencies may be related to parental genetics. Inbreeding of the stock culture may be expected to result in increased expression of recessive characteristics, including morphological abnormalities with a heritable genetic basis. Evidence that this may be a relevant factor was provided by deformity incidence monitoring of the stock culture prior to the experiments with EMS.

A trend to increasing deformity incidence between the fourth and sixth generations in captivity was suggested (Figure 3). The experiments with EMS were conducted with fifth and sixth generation stock. Batac-Catalan and White (1982) recommend replacement of stock cultures every seven generations in order to ensure culture productivity, but do not discuss morphological condition.

Other explanations for high control deformity levels may include temperature, physical or crowding effects. Temperature control was lost at one point in the chronic toxicity experiments, which may have influenced deformity frequencies reported for controls A and B and 50 mg/L exposures. Temperature fell overnight from 20°C to about 3°C. Townsend et al. (1981) report hatching failure at a temperature of 8°C throughout embryonic development, and Sadler (1935) reports developmental arrest in 4th instar at constant temperatures less than 8°C.

Physical effects may be associated with the substrate material or food used for laboratory culture. Both are probably coarser and harder than natural substrates and foods, and may be abrasive to chironomid mouthparts.

Crowding within the culture may also influence development, through general developmental rate effects, although there is no evidence to suggest a specific influence on mouthpart morphology. Initial egg densities in the experimental cultures were 5 to 10 times those recommended by Townsend et al. (1981), although Townsend does not specifically mention density effects on survival.

Finally, the higher incidence of deformities in experimental controls than in unpolluted field locations may be related to stronger natural selection against mouthpart deformities in field situations. Natural selective pressures related to mouthpart morphology of chironomids are virtually unknown.

Reproductive Effects in Adults

Males from exposed cultures at 75 mg/L and 100 mg/L were mated with virgin females from control cultures in order to determined reporductive success. Exposed males and exposed females were mated at 50 mg/L. The numbers of matings attempted and the number of egg masses obtained at each dose level are summarized in Table 6. Only the egg masses produced at 50 mg/L were viable.

Virgin females do not lay eggs (Townsend et al., 1981). Thus, the females producing eggs at 75 mg/L and 100 mg/L were inseminated by EMS exposed males, the only males with which they had come in contact. The lack of embryonic development could be due either to male infertility, or to expression of dominant lethal mutations from the male genome. We cannot distinguish between these alternatives since the early embryo was not examined microscopically for evidence of cell formation. Gene expression in an insect embryo begins in the syncytial blastoderm stage after nuclear migration but prior to cell formation (Marx, 1984). In Chironomus, this period lasts for about four hours after nuclear migration (Yajima, 1964).

Males exposed to EMS at 50 mg/L were fertile, as were females, although the level of mouthpart deformities in their offspring suggests that some genetic damage to the germ cells may have occurred. This mating was not designed to distinguish between male and female parental effects.

CONCLUSIONS

It has been demonstrated that hypostomial plate deformities similar to those seen in chironomids from polluted environments can be induced by a genotoxicant in the laboratory. This suggests a genetic basis for observed deformities. However, a number of questions pertinent to the interpretation of chironomid morphology as a sediment quality indicator remain to be answered. In particular:

1. To what extent are induced deformities heritable? While deformities induced at higher dose levels of EMS were not heritable due to poor emergence and reproductive inhibition, heritable effects may be induced at lower dose levels. These effects require further study since heritability and persistence of deformities in natural populations influence the temporal resolution of the system for in situ sediment quality monitoring.
2. Can physical damage in early instars produce deformities in 4th instar larvae which resemble those induced chemically? While obvious physical damage was rarely observed in 4th instar larvae, molting may obscure the physical nature of early instar damage, without eliminating the defect. Thus, studies of factors producing physical damage and of damage transmission between instars are warranted.

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TABLE 1: CHRONIC EMBRYO-LARVAL TOXICITY OF EMS

	Nominal[1] Concentration of EMS (mg/L)											
	0 (Control)		50		100		500		1,000		5,000	
	A	B	A	B	A	B	A	B	A	B	A	B
Approximate[2] Initial No. of Eggs	1,725	1,750	1,425	2,075	2,025	2,275	2,300	2,050	1,900	2,275	2,325	1,700
Hatching Observed	+	+	+	+	+	+	+	+	-	-	-	-
2nd Instar Observed	+	+	+	+	+	+	-	-	-	-	-	-
Approximate Survival to 4th Instar[3] (%)	20	26	19	12*	23	15	0	0	0	0	0	0

[1] EMS degrades in water with a four-day half-life at 20°C; solutions were replaced every three days.

[2] Based on a count of 1/10th of the length of each egg string.

[3] Based on counts of 3rd and 4th instar larvae at an endpoint marked by the first appearance of pupae.

* Emergence and mating was allowed in 50 mg/L culture B; thus, it was not preserved concurrently with the other cultures.

TABLE 2: LARVAE SURVIVING AND ADULTS EMERGING FROM CULTURES EXAMINED FOR DEFORMITY INDUCTION

EMS Concentration (mg/L)	Approximate Initial No. of Eggs	No. of Organisms at Preservation					% Survival
		2nd Instar Larvae	3rd Instar Larvae	4th Instar Larvae	Pupae	Adults*	
Replicate No. 1 (preserved 7 days in advance of replicate No.2)							
0	1,175	-	791	100	5	40	80
75	1,275	8	608	163	2	5	62
100	1,475	3	17	39	26	2	6
240	1,725	-	-	108	47	-	9
Replicate No. 2							
0	1,775	-	-	70	1	800	49
75	1,500	-	71	116	33	2	15
100	1,425	-	5	19	5	3	2
240	2,125	-	-	28	2	-	1

* Including adults removed alive prior to culture preservation.

TABLE 3: MEAN WEIGHT OF 4TH INSTAR LARVAE EXAMINED FOR DEFORMITY INDUCTION

EMS Concentration (mg/L)	Replicate Number	Approximate Initial No. of Eggs	No. of 4th Instar Larvae	Mean Larval Weight (mg)
0	1*	1,175	100	6.6
	2	1,775	70	11.1
75	1*	1,275	163	13.1
	2	1,500	116	13.4
100	1*	1,475	39	23.8
	2	1,425	19	20.5
240	1*	1,725	108	13.9
	2	2,125	28	**

* Replicate 1 was preserved 7 days in advance of replicate 2.

** Larvae not weighed prior to mounting.

TABLE 4: INCIDENCE OF MOUTHPART DEFORMITIES IN RELATION TO EMS EXPOSURE LEVEL

EMS Concentration (mg/L)	Replicate Number[1]	No. of 4th Instar Larvae Examined	No. of Larvae Deformed	% Deformed
0	A	100	14	14
	B	100	6	6
0	1*	95	19	20
	2	67	14	21
50	A	96	13	14
	B	99	13	13
75	1*	100	13	13
	2	99	30	30
100	1*	39	14	36
	2	19	8	42
240	1*	92	42	46
	2	28	14	50

[1] Cultures labelled A and B were initiated in preliminary toxicity determinations; those labelled 1 and 2 were initiated 30 days later.

* Replicate 1 was preserved 7 days in advance of replicate 2.

TABLE 5: TYPES OF DEFORMITIES OBSERVED IN 4TH INSTAR LARVAE EXPOSED TO EMS

	Percentage[1] of Deformed Larvae[2] in Each Category											
	Control		Control		50 mg/L		75 mg/L		100 mg/L		240 mg/L	
	A	B	1	2	A	B	1	2	1	2	1	2
Type of Deformity	(14)	(6)	(19)	(14)	(13)	(13)	(13)	(30)	(14)	(8)	(42)	(14)[2]
1. Missing or fused lateral teeth	43	-	5	29	15	23	69	53	43	63	26	7
2. Extra lateral teeth	7	-	5	-	-	-	15	-	7	-	-	-
3. Koehn gap	-	-	-	-	8	-	-	-	7	-	-	7
4. Abnormal[3] median tooth	50	83	84*	14	62	38	15	40	21	75	60	71
5. Abnormal[3] first lateral tooth	-	33	16	57**	38	62	8	13	36	-	14	29

[1] Column sums of percentages may exceed 100% since some larvae displayed multiple types of abnormalities.

[2] Numbers in parentheses indicate number of larvae deformed.

[3] Abnormalities of the median tooth (normally trifid) and first lateral tooth (normally bifid) include fusion of processes or extra processes.

* Cleft median tooth common in Control 1.

** Symmetrical partial fusion of processes on the first lateral common in Control 2.

TABLE 6: REPRODUCTIVE SUCCESS OF MALE CHIRONOMIDS FROM EMS-EXPOSED CULTURES

EMS Concentration (mg/L)	No. of Matings of Exposed Males to Single Females	Females Exposed/ Unexposed	No. of Egg Masses Obtained	No. of Egg Masses Viable
0	4	unexposed	4	4
50	2	exposed	2	2
75	5	unexposed	1	0
100	2	unexposed	2	0

FIGURE I Normal Morphology of the Hypostomial Plate in *Chironomus*

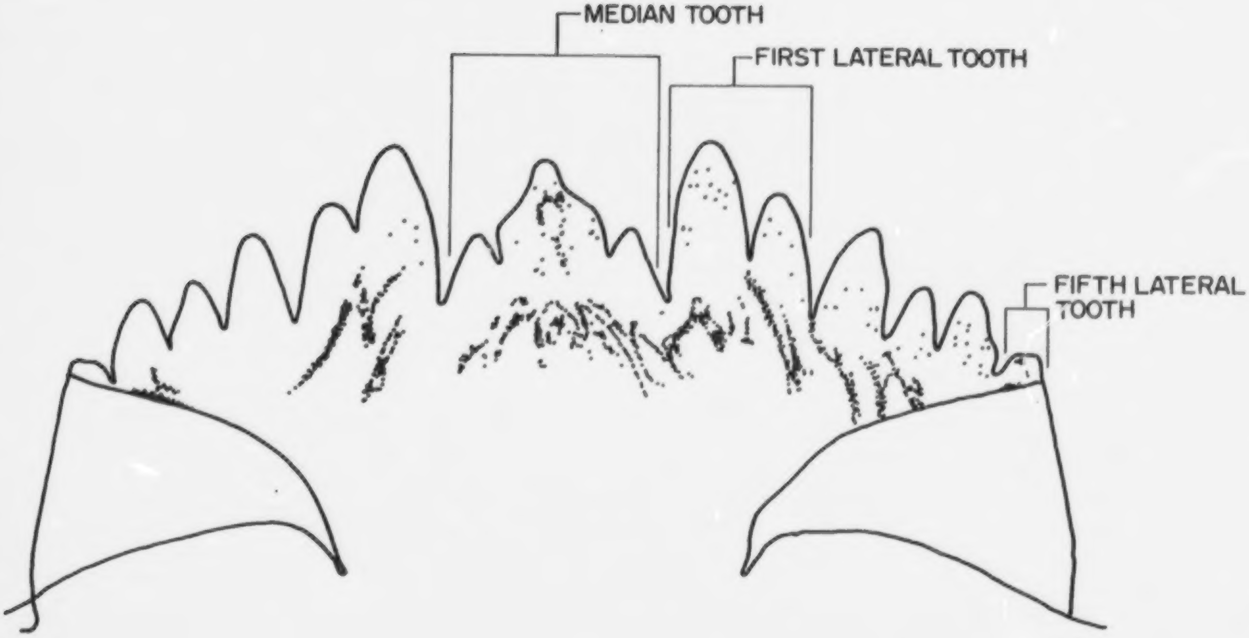

MEDIAN TOOTH
FIRST LATERAL TOOTH
FIFTH LATERAL TOOTH

FIGURE 2 Relationship of Mouthpart Deformities to EMS Exposure

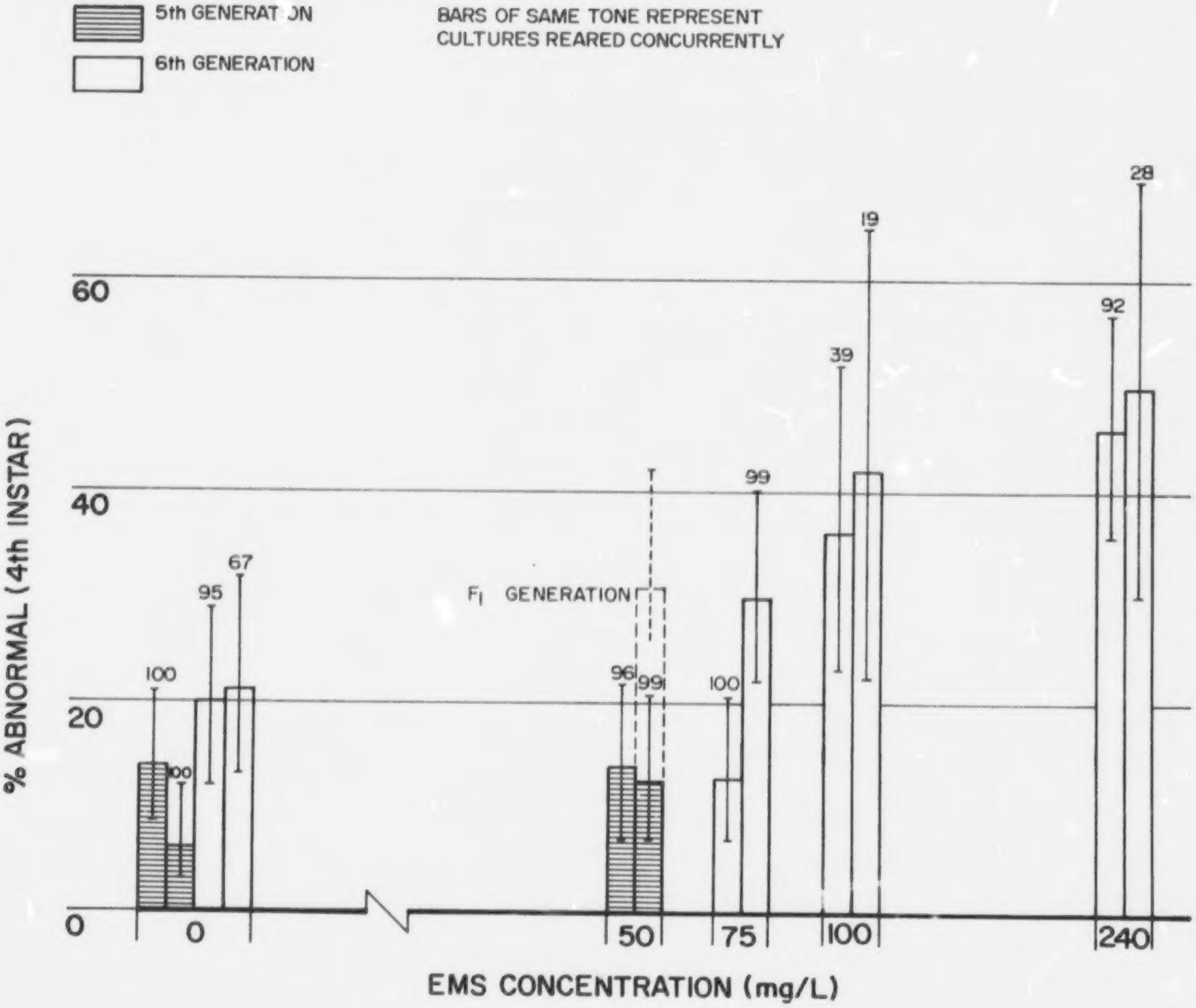
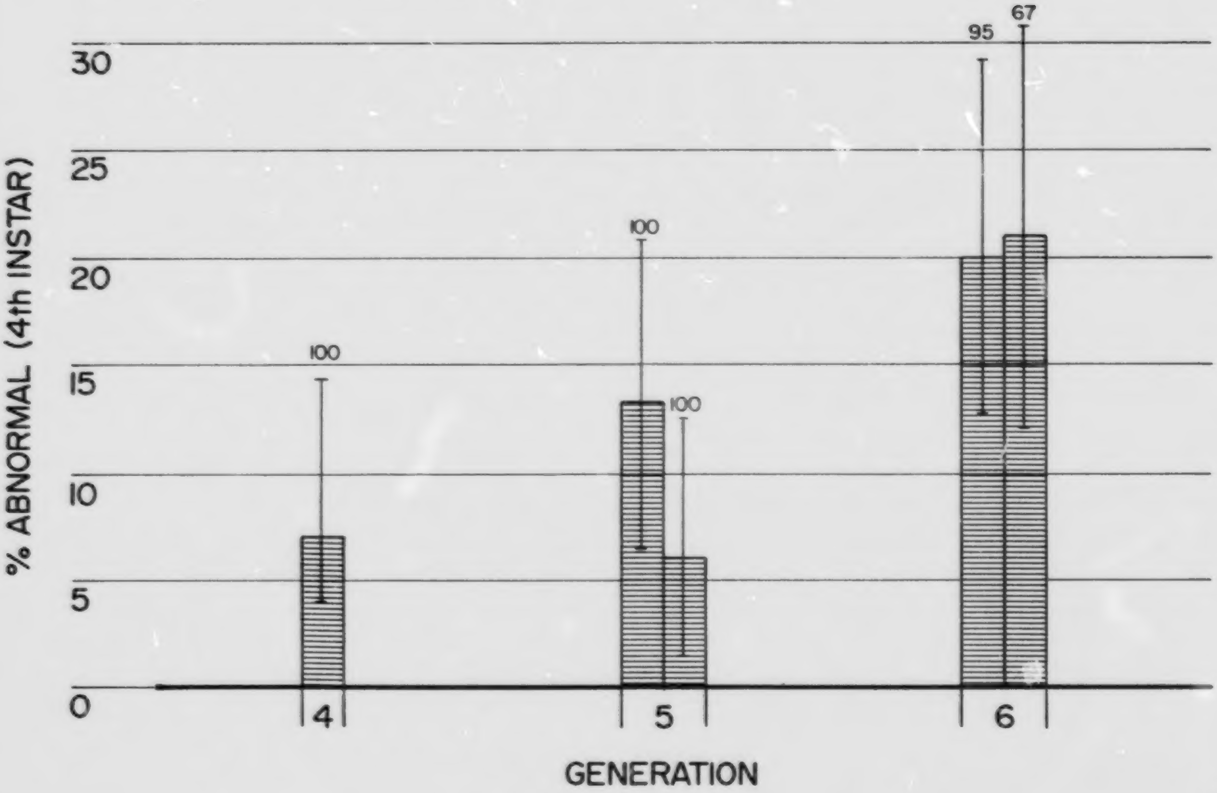


FIGURE 3 Control Deformity Incidence in Successive Laboratory Generations



Freshwater clams as monitors of variation in environmental acidity and trace metal levels

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Summary

We collected freshwater clams (*Elliptio complanata*) from an acid sensitive and a circumneutral lake in south-central Ontario and compared tissue metal concentrations. Clams from the circumneutral lake had greater concentrations of Zn and Mn and lower concentrations of Cu and Cd than clams from the acid sensitive lake. Clam size and/or age successfully predicted tissue metal levels, suggesting that long-term clam biomonitoring studies should control for size and age variability.

We examined the effects of environmental acidity on *E. complanata* shell morphology and concluded that differences in shell size and shape were a function of within-lake variation in water turbulence. Therefore the use of shell morphology as an indicator of environmental acidification requires prior consideration of within-lake variability in shell form.

Clam shells were not useful monitors of environmental trace metal levels.

Introduction

Molluscs have, for over 10 years, been used to monitor contaminant levels in the marine environment (Goldberg et al. 1978). They accumulate and concentrate a wide range of environmentally available pollutants, and they are widely distributed both globally and in terms of the habitats that they occupy (Green et al. 1985). In recent years, freshwater clams have been used to monitor variation in environmental contaminant levels through *in situ* (Forester 1980; Imlay 1982; G.L.I. 1984; Pugsley et al. 1985) and transplantation (Kauss et al. 1981; G.L.I. 1985) studies. It is uncertain, however, whether freshwater clams exhibit size- and age-specific contaminant accumulation patterns similar to their marine counterparts (Boyden 1977; Romeril 1979; Cossa et al. 1980). This must be determined before freshwater clams are extensively used as biomonitors. In this study we examine size- and age-specific patterns of trace metal concentrations in the freshwater clam *Elliptio complanata*.

The bioavailability of many trace metals is enhanced by increasing environmental acidity (Campbell et al. 1983; Campbell and Stokes 1985; Stokes et al. 1985; Kelso et al. 1986). In acid stressed, poorly buffered waters, bioaccumulation of trace metals has been reported in clams (Forester 1980; Graney et al 1984). We will compare tissue metal concentrations in *E. complanata* from an acid sensitive and a circumneutral lake. The relative importance of these patterns will be examined by comparing them to the size- and age-specific relationships.

Although clam tissues are useful for monitoring short-term fluctuations in aquatic contaminant levels, clam shells may be useful as indicators of long-term water quality patterns. It has been suggested that variation in environmental acidity can cause variation in shell shape (Mackie and Flippance 1983) and growth rate (Green 1980; Singer 1981) because calcium, which is necessary for shell growth, is often less available in low alkalinity environments. We examined this hypothesis by sampling _E. complanata_ from four small lakes that vary in alkalinity and compared within-lake to between-lake variation in shell morphology.

Marine clam shells can retain a record of contaminant levels over many years (Fang and Shen 1984), so clam shells may provide a more long-term and irreversible system for monitoring changes in environmental levels of trace metals than clam tissues. We utilized the electron probe and the secondary ion mass spectrometer to assess trace metal levels in thin sections of freshwater clam shells sampled from known contaminated areas.

Methods

Age- and size-specific trace metal patterns

We collected 50 _E. complanata_, including as wide a size range as possible, from the southwest corners of Beech Lake and Tock Lake using SCUBA. These lakes are located in south-central Ontario on the Precambrian Shield (Fig. 1). Although morphologically similar, the lakes vary greatly in alkalinity with total inflection point alkalinities for Tock and Beech of 22 and 153 ueq/l respectively. Shell lengths were determined and used as a measure of clam size. Clam tissues were dissected into gill and remaining visceral mass (body), then dried and digested in concentrated nitric acid, and analyzed using flame spectrophotometry for levels of Cu, Cd, Zn, and Mn. Shells were aged by the thin-section method (Clark 1980).

Analysis of variance (ANOVA) was used to compare differences in gill and body trace metal concentrations between the lakes. Analysis of covariance (ANCOVA) was used to compare the relationships between clam age and length and tissue metal concentration. Tissue metal concentration and length data were log-transformed , prior to analysis, to reduce error variance heterogeneity.

Within- and between-lake variation in shell form

We collected 25 *E. complanata* using SCUBA from a low (southwest) and a high (northeast) exposure site (i.e. water turbulence) in each of four small lakes (Figs. 1 and 2). Only old individuals were collected to eliminate age structure as a confounding factor. Shell length, height, width and weight were determined (Fig. 3). These data were log-transformed to linearize allometric relationships between the variables.

A model II ANOVA estimated the proportion of the total variance of each variable due to variation between the four lakes, between exposure levels within the lakes and between individual clams within the sites.

Shell analysis for trace metals

Thin sections of clam shells were prepared for the electron probe following the methods of Lutz (1981). As, Hg, Pb, Cd, Ca, Sb and Zn levels can be determined by the characteristic x-rays which are emitted from the thin section when an electron beam is focussed on it. The secondary ion mass spectrometer, which is a more sensitive instrument than the electron probe, was also used to determine levels of the same metals in the thin sections.

Results

Age- and size-specific trace metal patterns

Trace metal concentrations in both gill and body tissues differed between Beech Lake and Tock Lake clams (Table 1). Tock Lake clam tissues were higher in Cu and Cd and lower in Zn and Mn than Beech Lake clam tissues ($P<0.05$). There was not any strong relationship between clam size and age possibly because of the lack of extremely small individuals in the sample. Size and age could therefore be used as independent covariates in each analysis. Each model (Table 2) was successful in predicting tissue trace metal variability from clam size and age.

Within- and between-lake variation in shell form

In Green, Beech, Bark and Tock Lakes, clams from the high exposure site had longer, taller, wider and heavier shells than those from the low exposure site (Table 3). Components of variance computed from the model II ANOVAs revealed that much more of the variation in shell morphology resulted from differences between exposures rather than differences between lakes (Fig. 4).

Shell analysis for trace metals

The electron probe analyses showed no detectable levels of As, Hg, Cd, Pb or Zn in the shells examined. The secondary ion mass spectrometer detected only major shell elements (i.e. Ca, C, Sr, Na, Fe, Mn) which were in part per thousand concentrations.

Discussion

Age- and size-specific trace metal patterns

Cu, Cd, Zn and Mn are known to increase in geochemical mobility with increasing acidification (Campbell et al. 1983) and are generally in greater concentrations in Ontario non-buffered versus buffered waters (Forester 1980). Tock Lake is acid sensitive and has low buffering capabilities while Beech Lake is circumneutral and thus possesses the ability to buffer fluctuating levels of acidic input. Analyses of a small number of water samples from these lakes (unpub. data) suggest that absolute levels are generally greater in Tock Lake. However, Beech Lake has greater Mn and Zn levels relative to Cu and Cd than does Tock Lake. Concentrations of metals in the clams showed similar patterns, as Beech Lake clams had higher Mn/Cu, Mn/Cd, Zn/Cu and Zn/Cd ratios. These results closely resemble those of Servos (pers. comm.; Freshwater Institute, Winnipeg Manitoba) who examined bioaccumulation of metals by E. complanata during acidic snowmelt. In his study, Zn concentrations increased relative to Cd concentrations in gill and body tissues as environmental acidity decreased.

There can be competition between metals for a limited supply of ligand (binding substrate) within marine mollusc tissue, and the competitive nature of metals for ligands can be altered depending on environmental metal levels (Mason and Simkiss 1983). It is thus possible that higher absolute metal levels (i.e. in Tock Lake) enhance the competitive nature of Cu and Cd for binding substrate while lowering that of Zn and Mn. Competition between trace metals for binding substrate in E. complanata tissues has been reported by Tessier et al. (1984) who determined that Fe competes with Cu and Zn. They suggested that Fe plays a protective role as it is the principal factor controlling the dissolved trace metal concentrations to which the clam is exposed.

Gill tissue metal concentrations were often twice that of body tissue. Gill concentrations may be overestimated and may not reflect biologically available metals, because available and non-available metals can adhere to mucous covered gill surfaces. Including gills in whole body analyses may therefore be inappropriate, because they could decrease the predictive power of the model by increasing body tissue trace metal variability.

Size- and age-specific trace metal relationships were different for each tissue type and each metal. This type of variability is common in marine bivalves (Boyden 1977; Romeril

1979; Cossa et al. 1980; Popham and D'Auria 1983). There are many factors which could enhance variability in these patterns such as feeding habits, reproductive state and condition factors. However, physiological explanations for the observed patterns are not within the scope of this paper. Size and age are important factors which contribute to tissue trace metal variability. Therefore, investigators who wish to compare *E. complanata* metal concentrations should standardize clam size and age. This would especially apply to clam biomonitoring studies where comparisons are made among sites and years.

In only two cases (gill Cu and body Cd) did lake interact with clam size and/or age in modelling tissue trace metal variability. Buffering capability, which is the primary difference between the two lakes, is therefore not very important in influencing size- and age-specific patterns. However, with only two lakes in the analyses, we have very little power to detect such an influence.

Within- and between-lake variation in shell form

Exposure affected variation in shell morphology similarly in all four lakes. Clams from low exposure sites were smaller and lighter than those from high exposure sites. These characteristics may be adaptive because small, light shells would preclude sinking in low exposure, soft silt areas while large, heavy shells would prevent dislodgement by wave action in high exposure, sandy areas.

Some researchers have suggested that variation in alkalinity can cause variation in clam growth patterns (Green 1980; Singer 1981; Mackie and Flippance 1983). However, interpretation of those studies is often difficult because within-lake variation in growth patterns was not considered. In this study, much more of the total variation in shell form was due to within-lake between-exposure differences rather than between-lake differences. The primary difference between the four lakes is alkalinity; therefore alkalinity has little to do with variation in _E. complanata_ shell form. Our results indicate that within-lake variation in shell form must first be assessed or controlled by the study design, before among-lake variation is examined.

Shell analysis for trace metals

The electron probe has a maximum sensitivity of 200 ppm, however, it could not detect As, Hg, Cd, Pb or Zn in the shells examined. Similar results were obtained from the more sensitive secondary ion mass spectrometer. Body tissue analyses of the same specimens had shown significant As, Hg and Pb concentrations (Metcalfe and Mudrock 1985).

Conclusions

Freshwater clam tissues can be a useful tool for monitoring _in situ_ levels of biologically available trace metals in areas affected by acidic precipitation once size and age effects are controlled for. Before large scale transplantation studies are designed, heritability of trace metal uptake rates should be examined. For example, Hinch et al. (1986) concluded that growth rates of the unionid clam *Lampsilis radiata* were a function of the population source (in a field transplant experiment). Other physiological processes which may be related to trace metal uptake may also be a function of the population source. A three-way reciprocal transplant experiment has been conducted using *E. complanata* and three lakes which represent the "degree of acidification" gradient. These data are presently being analysed. Electrophoretic studies in allozyme frequencies are being done, to investigate the role of genotype in trace metal uptake.

Although clam shells have proven to be useful monitors of contaminant levels in marine environments, they were not useful for monitoring levels of trace metals at the environmental concentrations observed in this study. Shell morphology is not a good predictor of environmental acidity but probably reflects site-specific water turbulence.

Acknowledgements

Linda Stephenson and Vicki Young prepared the clam tissues for metal analysis and the shells for aging. Cindy Walker prepared and analyzed shell sections for trace metals. Robert Bailey commented on earlier drafts of this paper. The Ontario Ministries of the Environment and Natural Resources, and Environment Canada provided important data for this study. This study was made possible through NSERC and Ontario Ministry of the Environment operating grants to R. H. Green, and an Ontario Graduate Scholarship awarded to S.G. Hinch.

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Table 1. Mean metal concentrations in p.p.m (SD) in gill and body tissues of *E. complanata* from Beech Lake and Tock Lake. Each Mn concentration is x 102.

		Beech Lake		Tock Lake	
gill	Cu	13.28	(5.69)	18.51	(7.83)
	Cd	10.10	(4.34)	12.78	(4.49)
	Zn	371.32	(108.75)	273.81	(72.80)
	Mn	140.80	(40.30)	104.90	(32.70)
body	Cu	7.29	(1.83)	10.29	(6.95)
	Cd	10.98	(5.82)	14.51	(4.62)
	Zn	155.50	(43.87)	134.17	(63.15)
	Mn	42.20	(19.60)	23.50	(12.00)

Table 2. ANCOVA models which predict tissue trace metal variability from clam size and age in Beech Lake and Bark Lake.

dependent variable: gill Cu
model r2=.34

source of variation	P
length	.106
age	.001
lake	<.001
length * age	.521
length * lake	.250
age * lake	.462
length * age * lake	.014

dependent variable: gill Cd
model r2=.18

source of variation	P
length	.002
age	.443
lake	.021
length * age	.457
length * lake	.737
age * lake	.170
length * age * lake	.456

dependent variable: gill Zn
model r2=.25

source of variation	P
length	.759
age	.003
lake	<.001
length * age	.642
length * lake	.378
age * lake	.278
length * age * lake	.403

dependent variable: gill Mn
model r2=.23

source of variation	P
length	.923
age	<.001
lake	<.001
length * age	.717
length * lake	.634
age * lake	.303
length * age * lake	.692

dependent variable: body Cu
model r2=.20

source of variation	P
length	.049
age	.073
lake	.004
length * age	.043
length * lake	.532
age * lake	.885
length * age * lake	.241

dependent variable: body Cd
model r2=.50

source of variation	P
length	<.001
age	.300
lake	<.001
length * age	.033
length * lake	.015
age * lake	.602
length * age * lake	.887

dependent variable: body Zn
model r2=.20

source of variation	P
length	.035
age	<.001
lake	.005
length * age	.739
length * lake	.598
age * lake	.952
length * age * lake	.727

dependent variable: body Mn
model r2=.42

source of variation	P
length	.119
age	<.001
lake	<.001
length * age	.911
length * lake	.549
age * lake	.261
length * age * lake	.406

Table 3. Means (SD) of shell characters from low and high exposure sites in the study lakes. In all groups n=25.

Site	Length (mm)	Height (mm)	Width (mm)	Weight (g)
Tock low	66.0 (5.4)	33.2 (2.7)	17.7 (1.9)	9.6 (2.9)
Tock high	74.1 (5.8)	37.2 (3.0)	19.6 (2.1)	14.1 (3.6)
Bark low	59.4 (4.5)	28.6 (1.8)	17.8 (1.5)	8.1 (2.0)
Bark high	64.2 (3.1)	30.9 (1.5)	19.4 (1.2)	10.8 (2.1)
Beech low	63.3 (6.3)	31.6 (3.5)	16.7 (2.4)	8.5 (2.8)
Beech high	72.1 (6.3)	36.6 (3.1)	19.7 (2.2)	13.6 (3.7)
Green low	63.0 (8.6)	31.1 (4.2)	16.2 (2.6)	8.8 (4.5)
Green high	66.9 (7.7)	33.1 (3.8)	17.7 (2.5)	11.0 (4.7)

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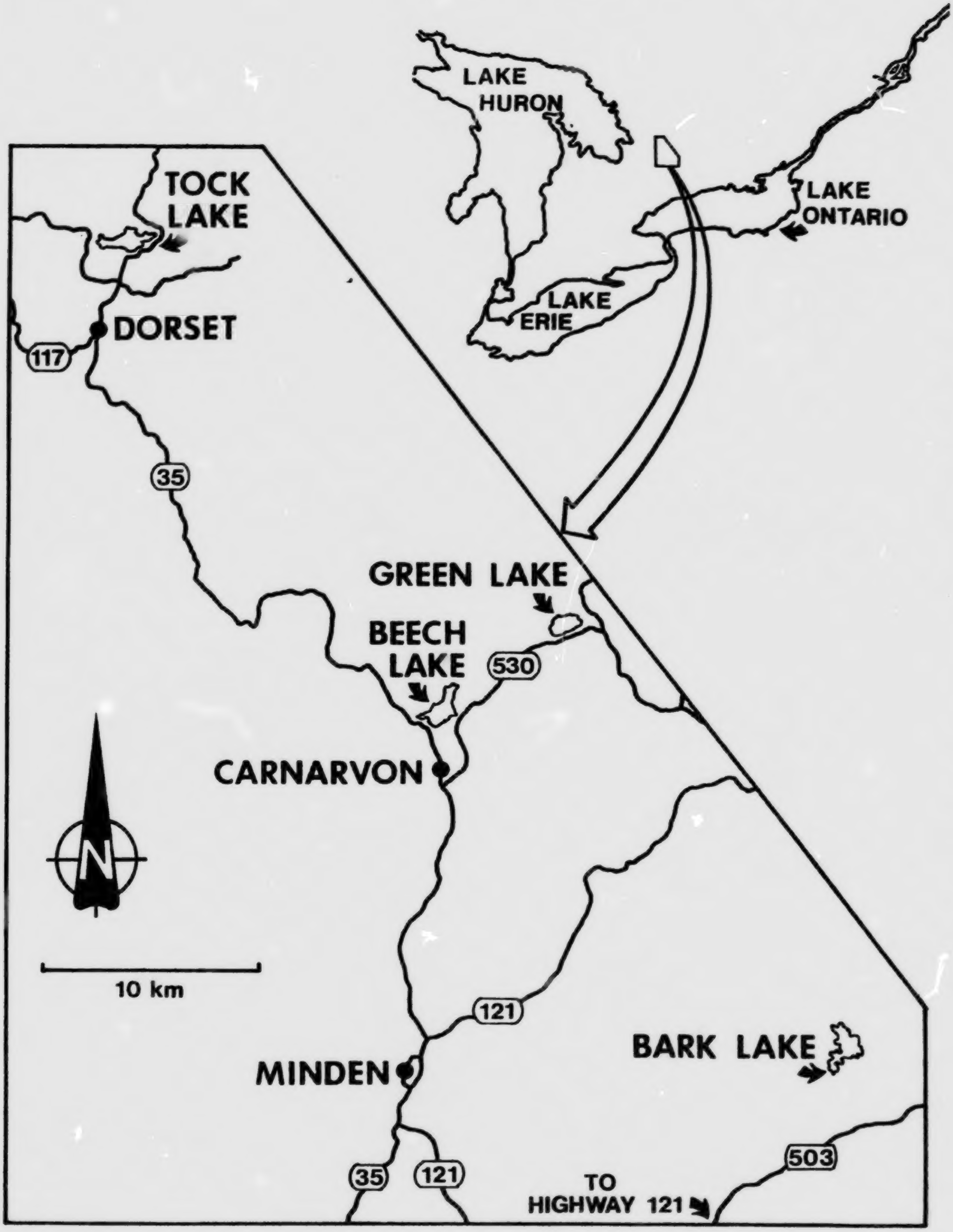
Fig. 1. Location of study area in south-central Ontario and detailed locations of lakes in relation to provincial highways and towns.

Fig. 2. Four study lakes with the low (L) and high (H) exposure sites in each lake.

Fig. 3. A drawing of Elliptio complanata (Unionidae) showing length, height and width dimensions.

Fig. 4. Proportions of total variance in shell height, length, weight and width due to variation among the four lakes, between exposure levels within the lakes and among individual clams within the sites.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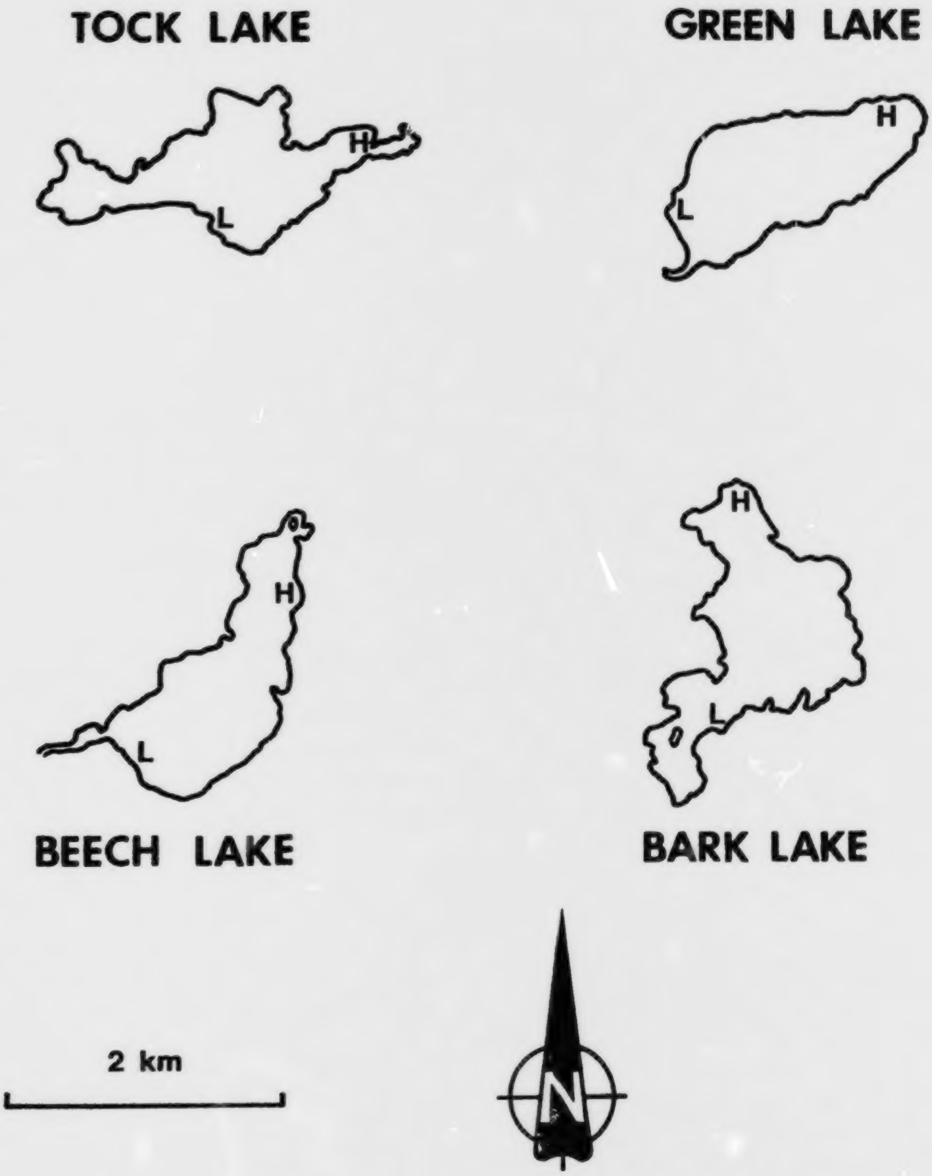
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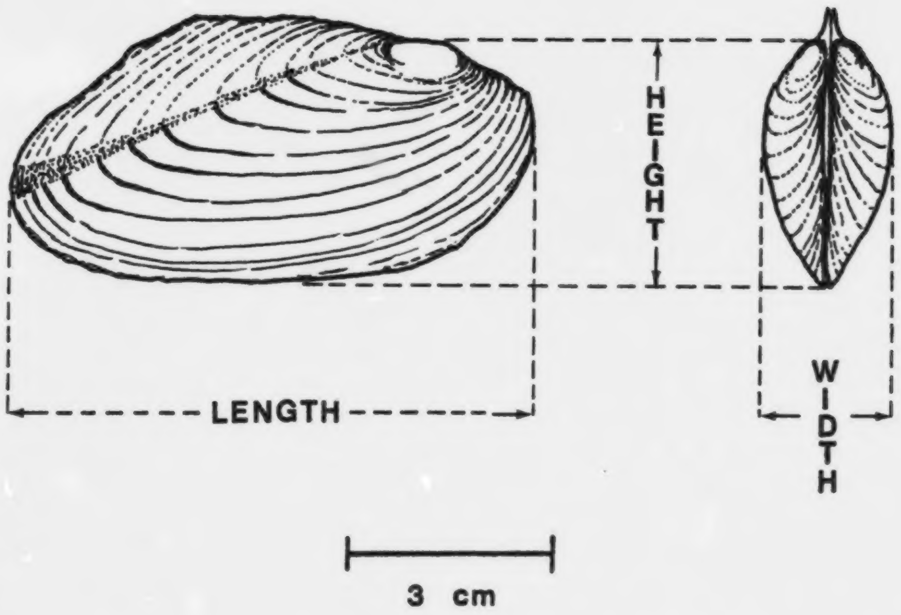
Elliptio complanata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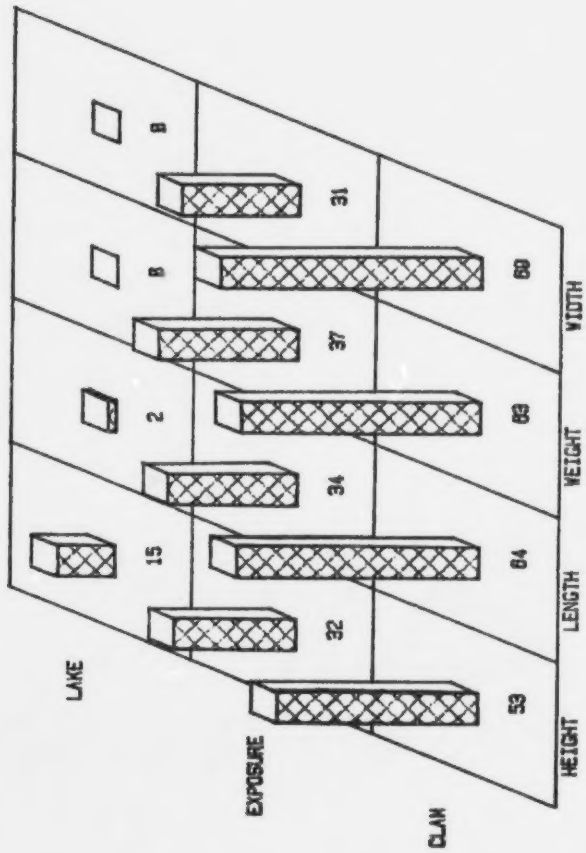
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60

ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA

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INTRODUCTION

The method currently used by the Ontario Ministry of the Environment for the determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) is based upon the procedure developed by Lamparski, Nestrick, and Stehl (1). The Dow procedure involves the use of multiple open-column chromatographic cleanup steps followed by fractionation on reverse phase HPLC in order to yield a sample suitable for analysis by GC/MS techniques. The analytical scheme employed by the Ministry of the Environment is outlined in figure 1. This procedure is tedious as well as time consuming. The cleanup method has been found to be ineffective for very complex samples, particularly for those containing high levels of polychlorinated biphenyls (PCB). In addition it is not possible to simultaneously determine other environmental pollutants because of poor recoveries or improper fractionation.

This study involves the development of a new cleanup procedure for the analysis of PCDD and PCDF in fish tissue. Work was carried out to devise an HPLC fractionation which would isolate the PCDD and PCDF from potential interferences found in biological samples such as fish. Fractionation of the sample by HPLC rather than open-column chromatography has several advantages. Preparation of chromatographic columns is tedious and consumes large amounts of both time and materials. HPLC allows for rapid and much more reproducible fractionation of sample components. The potential of automated sample injection, data acquisition, and fraction collection makes HPLC techniques even more attractive.

The HPLC method developed to replace the column chromatography cleanup consists of a two-step fractionation procedure. The PCDD and PCDF are initially isolated from the bulk of the sample matrix using normal phase HPLC. A second fractionation is then carried out on reverse phase HPLC to further isolate the PCDD and PCDF from any interferences which were coeluted during the normal phase separation. Additional fractions may be collected in the first fractionation step if other sample components are to be analyzed. The overall analytical scheme for the analysis of PCDD and PCDF in fish is represented in figure 2.

EXPERIMENTAL

Instrumentation:

All HPLC fractionations were carried out using a Varian Model 5000 liquid chromatograph equipped with a fixed wavelength (254 nm) ultraviolet detector. The chromatographic injection system consisted of a Rheodyne pneumatic valve with a 100 uL loop injector. A Vista chromatography data system was interfaced to the HPLC allowing both manipulation of HPLC parameters and raw data collection on floppy disk. Normal phase fractionations were obtained using a semi-preparative scale silica column (25 x 0.94 cm) containing 10 um particles. The gradient elution program employed in the normal phase separation is shown in figure 3. A Micro-Pak MCH-10 ODS reverse phase column (30 x 0.94 cm, 10 um particles) was used for the second fractionation step. The reverse phase gradient elution program is illustrated in figure 4.

A Hewlett-Packard HP5987A GC/MS with an HP1000 data system and HP7914 disk drive was used for mass spectral analysis. An HP5880A gas chromatograph is directly interfaced to the quadrupole mass spectrometer by a capillary inlet. The chromatographic column used was a 30 meter DB-5 fused silica capillary column (0.25 mm i.d.) having a stationary film thickness of 0.25 um. All GC/MS analyses were made using a cool on-column injector to minimize discrimination against compounds with high boiling points and also provide efficient sample loading onto the column.

Chemicals and Solvents:

Organic solvents used in this study were hexane, benzene, dichloromethane, and methanol. All solvents were distilled in glass and are suitable for pesticide analysis (Caledon Laboratories Ltd., Georgetown, Ontario). Water for the reverse phase HPLC fractionation was distilled using a Kontes still (Vineland, New Jersey).

Reagent grade anhydrous sodium sulphate (J.T. Baker Chemical Co., Phillipsburg, New Jersey) was washed with 50 mL of hexane prior to use but was otherwise used in the form obtained by the supplier.

Dibenzodioxin and dibenzofuran standards were supplied by the Ministry of the Environment and also obtained directly from Cambridge Isotopes Laboratories (Woburn, Massachusetts). Analytical standards for other pollutants such as PCB, chlorinated pesticides, and polycyclic aromatic hydrocarbons (PAH) were obtained from a variety of sources.

Glassware Cleaning:

All glassware was cleaned by ultrasonic agitation in a water bath containing a mild detergent. Individual pieces were then thoroughly rinsed with deionized water and dried at 250°C overnight. All glass apparatus was rinsed three times with an appropriate organic solvent immediately prior to use.

HPLC Mobile Phase Preparation:

Solvents employed as HPLC mobile phases were filtered and degassed before use. Solvent filtration was achieved using a clarification kit consisting of a one-litre flask and 300 mL filter reservoir which is fitted with a replaceable 0.45 um HVLP filter (Waters Millipore, Milford, Massachusetts). Following filtration each solvent was then deaerated by application of a vacuum and mechanical stirring.

Sample Preparation Prior to Normal Phase HPLC Fractionation:

Fish tissue extracts were obtained from the Ministry of the Environment and only required concentration prior to HPLC fractionation. Initial sample preparation carried out by Ministry personnel was as follows: Fish tissue is homogenized and then transferred to a clean, dry glass jar. Twenty grams of tissue is placed into an erlenmeyer flask to which 70 mL of concentrated hydrochloric acid is added. The tissue is allowed to digest at room temperature for at least 16 hours. The resulting mixture is extracted with three 50 mL aliquots of hexane. The combined organic extract is then concentrated to approximately 20 mL.

Before the fish tissue extract can be fractionated by HPLC, it is necessary to perform a preliminary cleanup step in which lipids and large polar molecules are removed. This is accomplished using a chromatographic column with sulphuric acid/silicic acid packing. This packing is made up by thoroughly mixing silicic acid (activated at 180°C) with sulphuric acid such that the resulting material is 44 percent H_2SO_4 by weight. Approximately 25 grams of the packing is placed in a glass column (100 x 10 mm i.d.) with a 100 mL reservoir. The column is pre-washed with 125 mL of hexane and then the sample is loaded onto the column with a disposable pipette. The desired organic components are eluted with 50 mL of hexane. The eluant is finally transferred to a clean glass vial where it is concentrated down to approximately 10 mL. The extracts were delivered in this form to our laboratory and the volumes were further reduced to 200 uL before injection on the HPLC.

PCDD and PCDF retention behaviour on normal phase HPLC was established using a flyash extract since it is a convenient source of all of the various isomers (2). This extract was obtained by the Soxhlet extraction of approximately 40 grams of municipal incinerator flyash (Toronto, Ontario) with 300 mL of benzene for 24 hours. The extract was then concentrated down to about 1 mL and loaded onto a Sep-Pak silica cartridge (Waters Millipore, Milford, Massachusetts) which had been pre-wet with 50 mL of hexane. A complex mixture of compounds including the PCDD and PCDF are eluted with 50 mL of hexane while the more polar constituents are retained on the cartridge. The organic extract is concentrated down to approximately 1 ml and transferred to a small glass vial. Finally the extract is concentrated to dryness under a gentle stream of high purity nitrogen (Union Carbide Canada Limited, Toronto, Ontario) and the residue is reconstituted with 200 uL of hexane.

Sample Preparation Prior to Reverse Phase HPLC Fractionation:

The components of all fractions collected during normal phase HPLC separation must be transferred into a solvent amenable to reverse phase HPLC before the second step fractionation can be carried out. This is accomplished by concentrating normal phase fractions to approximately 1 mL and transferring the extract to a glass vial where it is gently evaporated to dryness. The resulting residue is then redissolved in 200 uL of 10:90 benzene:methanol and is now ready for reverse phase HPLC.

Sample Preparation Prior to GC/MS Analysis:

The end-product of the two-step HPLC cleanup procedure is a solution containing the PCDD and PCDF along with numerous other compounds. The solvent matrix consists of a mixture of methanol and water (less than 10 percent) and therefore cannot be directly concentrated to yield a sample which can be chromatographed on the average capillary GC column. Therefore the PCDD and PCDF must be transferred to a solvent which is better suited to the application of GC techniques. This is done by extracting the reverse phase fractions with three 50 mL portions of hexane in a 250 mL separatory funnel. Each hexane extract is passed through a sintered glass filter containing approximately 10 grams of anhydrous sodium sulphate (pre-washed with 50 mL of hexane) and collected in a round bottom flask. The combined extracts are then concentrated to approximately 1 mL and transferred to small glass vials. Each extract is then evaporated to dryness under a stream of high purity nitrogen and finally redissolved in 100 uL of benzene. The sample extracts are now ready for analysis by GC/MS.

RESULTS AND DISCUSSION

Initial development of HPLC fractionation methodology involved the use of several standards containing compounds characteristic of those found in fish tissue, including compounds such as PCDD, PCDF, PCB, PAH, and chlorinated pesticides. Preliminary optimization of the HPLC fractionations was accomplished based upon the comparison of the retention behaviour of two dioxins isomers with the other compound classes mentioned above. The 1,2,3,4-tetrachloro- and octachlorodibenzodioxin isomers (1,2,3,4-TCDD and OCDD respectively) were chosen to represent all PCDD and PCDF because they represent the extremes in degree of chlorination for the isomers normally determined. Also, sufficient amounts of each were available to create solutions concentrated enough to be detected by the UV detector of the HPLC. These solutions can later be used to verify the reproducibility of HPLC retention times to permit proper fraction collection times. Figures 5b and 6b show the HPLC traces of 1,2,3,4-TCDD and OCDD under the optimized gradient programs for normal and reverse phase HPLC respectively.

In order to confirm retention behaviour of PCDD and PCDF on both normal and reverse phase HPLC, a solution containing all of the different isomers must be injected on the HPLC and numerous fractions collected. These fractions are then analyzed by GC/MS using selected ion monitoring techniques. Four ions were monitored for each congener group to permit positive identification of the PCDD and PCDF. Since there was no standard available which contained all of the PCDD and PCDF isomers, a flyash extract was used. This extract contains an easily detectable amount of dioxins and furans with relatively few interfering compounds being present. Since the levels of PCDD and PCDF in fish tissue are often extremely low and in fact may be below instrumental detection limits, it is not possible to use tissue extracts to determine HPLC retention behaviour.

Since fish tissue often contains many compounds which interfere with the GC/MS determination of PCDD and PCDF, the effectiveness of the HPLC cleanup procedure had to be investigated. This was accomplished by determining the effect of introducing a potentially interfering matrix to flyash extract and comparing the reconstructed ion chromatograms of the fortified and nonfortified extract. Two fortified flyash extracts were prepared; the first extract was spiked with a relatively large amount of various Aroclor standards while the second was fortified with a typical fish tissue extract. The concentration of individual Aroclors in the fortified extract were: Aroclor 1016, 7 ug/uL; Aroclor 1242, 14 ug/uL; Aroclor 1254, 5 ug/uL; and Aroclor 1260, 8 ug/uL. The flyash extract and the two fortified extracts were chromatographed under identical HPLC conditions and a single fraction containing the PCDD and PCDF was collected for each. The HPLC traces for the normal and reverse phase separations along with the fraction collection times are given in figures 7 and 8.

In the normal phase fractionation step, most of the PCB elute within the retention window of the PCDD and PCDF as can be seen by comparing parts a and b of figure 7. Therefore the first step fractionation procedure does not isolate the dioxins and furans from the potential interference from chlorinated biphenyls. However, the second step reverse phase fractionation does separate PCDD and PCDF from PCB. Figures 6b and 6c show that 1,2,3,4-TCDD and OCDD are well separated from the bulk of the PCB. A comparison of figures 8a and 8b reveals the effect of the addition of a large amount of PCB on the acquired separation. Clearly the majority of the chlorinated biphenyls are eluted quite early and the sections of the UV trace corresponding to the retention windows for PCDD and PCDF are virtually identical for the nonfortified and PCB-fortified flyash extract. Similiarly the HPLC traces for the flyash and flyash-fish extracts (figure 8a and 8c respectively) are virtually identical with respect the appearance of the traces within the fraction collection windows. The effectiveness of the separation obtained by employing the two-step HPLC cleanup procedure was confirmed by GC/MS. The reconstructed ion chromatograms for the individual congener groups of the PCDD and PCDF were found to be relatively free of interferences. Therefore the developed HPLC method appears to provide a reasonable cleanup which will aid in the determination and dioxins and furans in fish tissue. This method should also be applicable to most other biological materials although the initial sample preparation procedure may require suitable modification.

References:

1. Lamparski, L.L.; Nestrick, T.J.; and Stehl, R.H.; Anal. Chem., 51(9), 1453-8, 1979.
2. Karasek, F.W. and Hutzinger,O.; Anal. Chem., 58(6), 633A-42A, 1986.

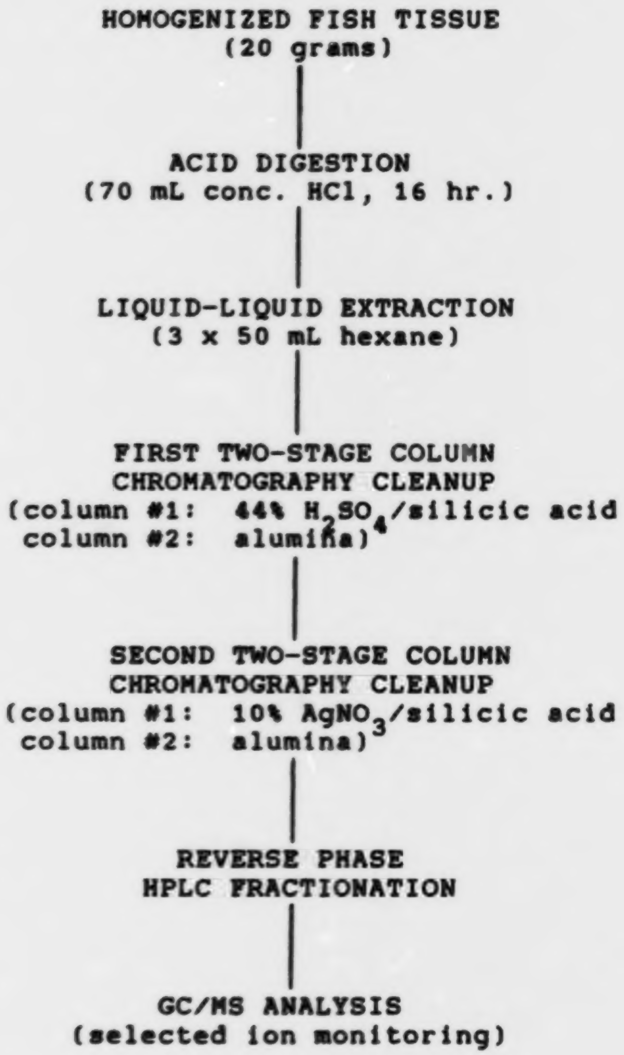
HOMOGENIZED FISH TISSUE
(20 grams)
ACID DIGESTION
(70 mL conc. HCl, 16 hr.)
LIQUID-LIQUID EXTRACTION
(3 x 50 mL hexane)
FIRST TWO-STAGE COLUMN
CHROMATOGRAPHY CLEANUP
(column #1: 44% H_2SO_4/silicic acid
column #2: alumina)
SECOND TWO-STAGE COLUMN
CHROMATOGRAPHY CLEANUP
(column #1: 10% $AgNO_3$/silicic acid
column #2: alumina)
REVERSE PHASE
HPLC FRACTIONATION
GC/MS ANALYSIS
(selected ion monitoring)

FIGURE I: Current MOE procedure for the analysis of PCDD and PCDF in fish.

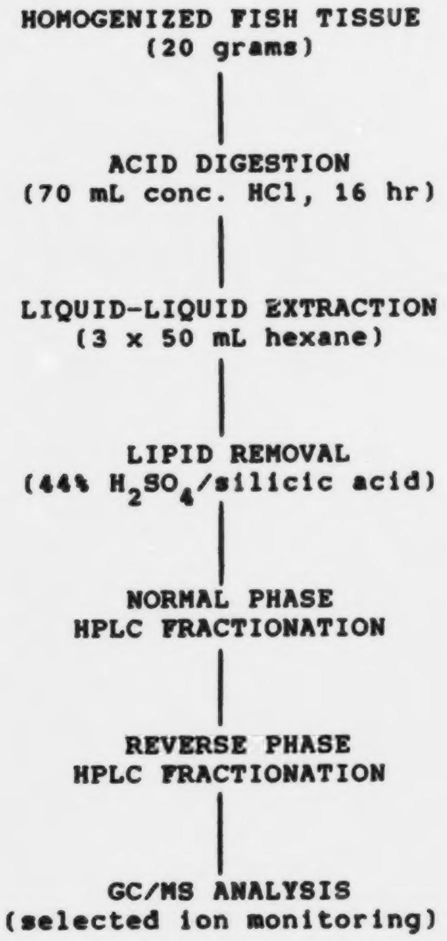
HOMOGENIZED FISH TISSUE
(20 grams)
ACID DIGESTION
(70 mL conc. HCl, 16 hr)
LIQUID-LIQUID EXTRACTION
(3 x 50 mL hexane)
LIPID REMOVAL
(44% H_2SO_4/silicic acid)
NORMAL PHASE
HPLC FRACTIONATION
REVERSE PHASE
HPLC FRACTIONATION
GC/MS ANALYSIS
(selected ion monitoring)

FIGURE 2: Proposed procedure for the analysis of PCDD and PCDF using a two-step HPLC fractionation.

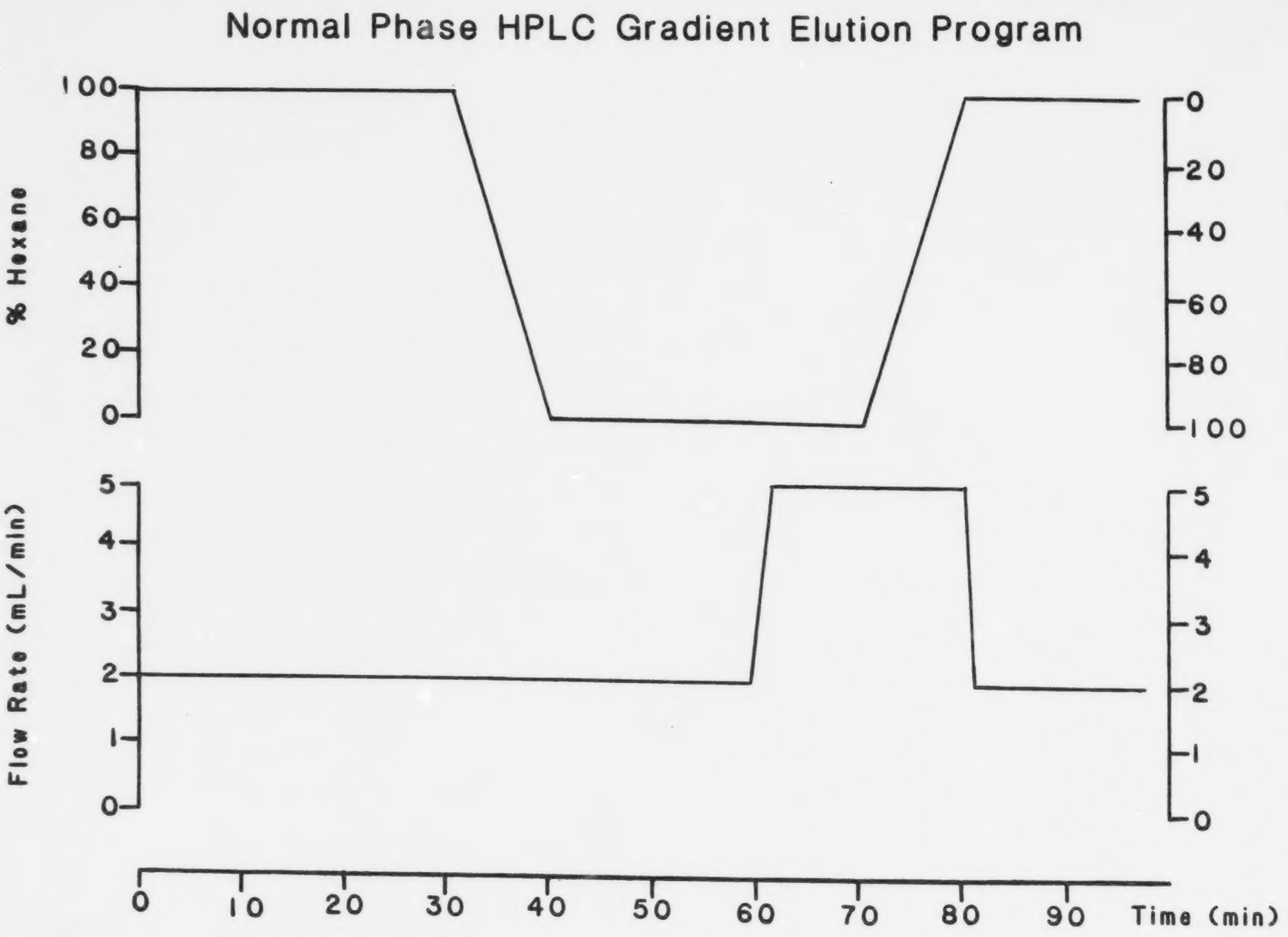

FIGURE 3: Mobile phase gradient elution program for normal phase HPLC.

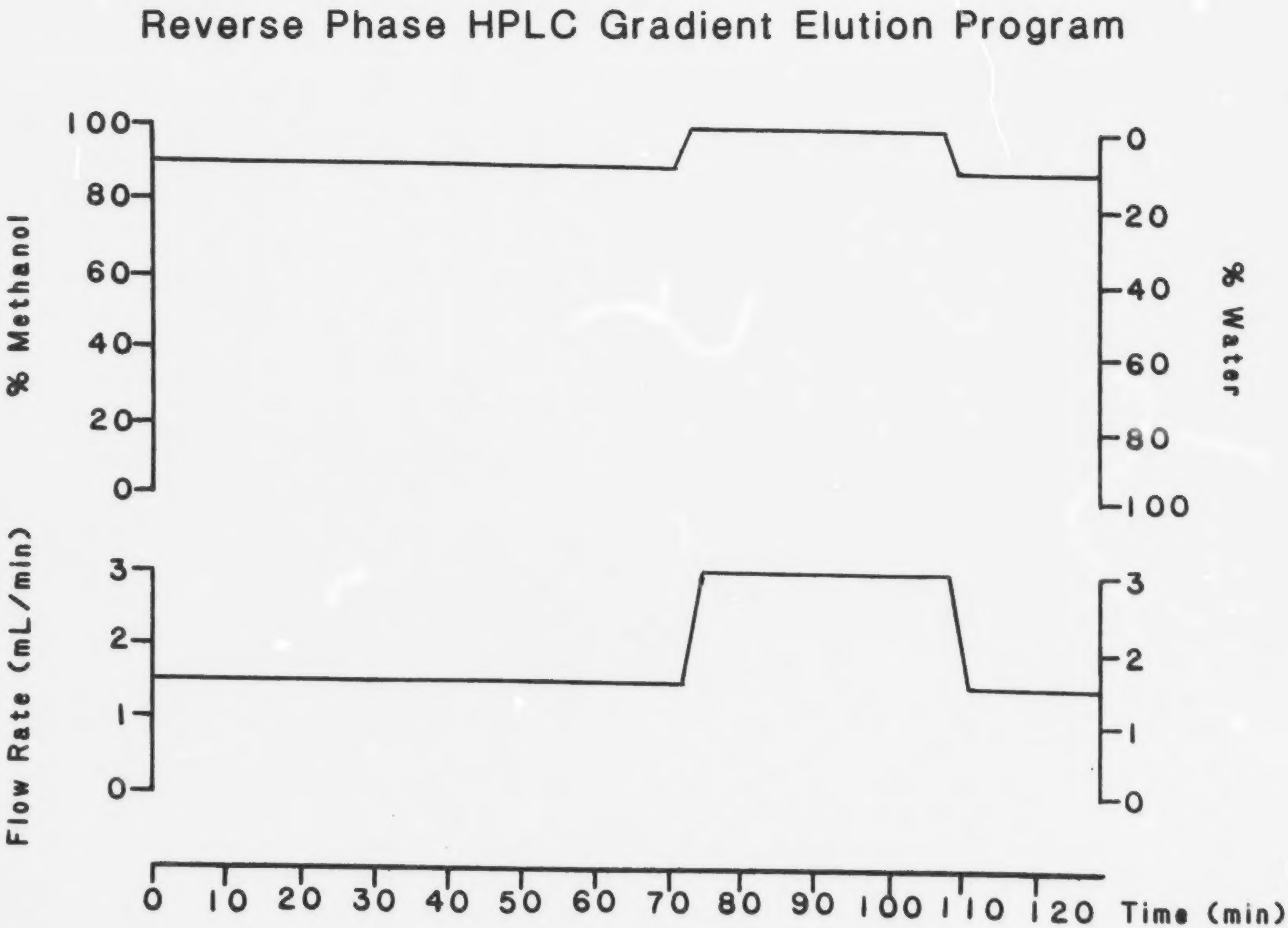

FIGURE 4: Mobile phase gradient elution program for reverse phase HPLC.

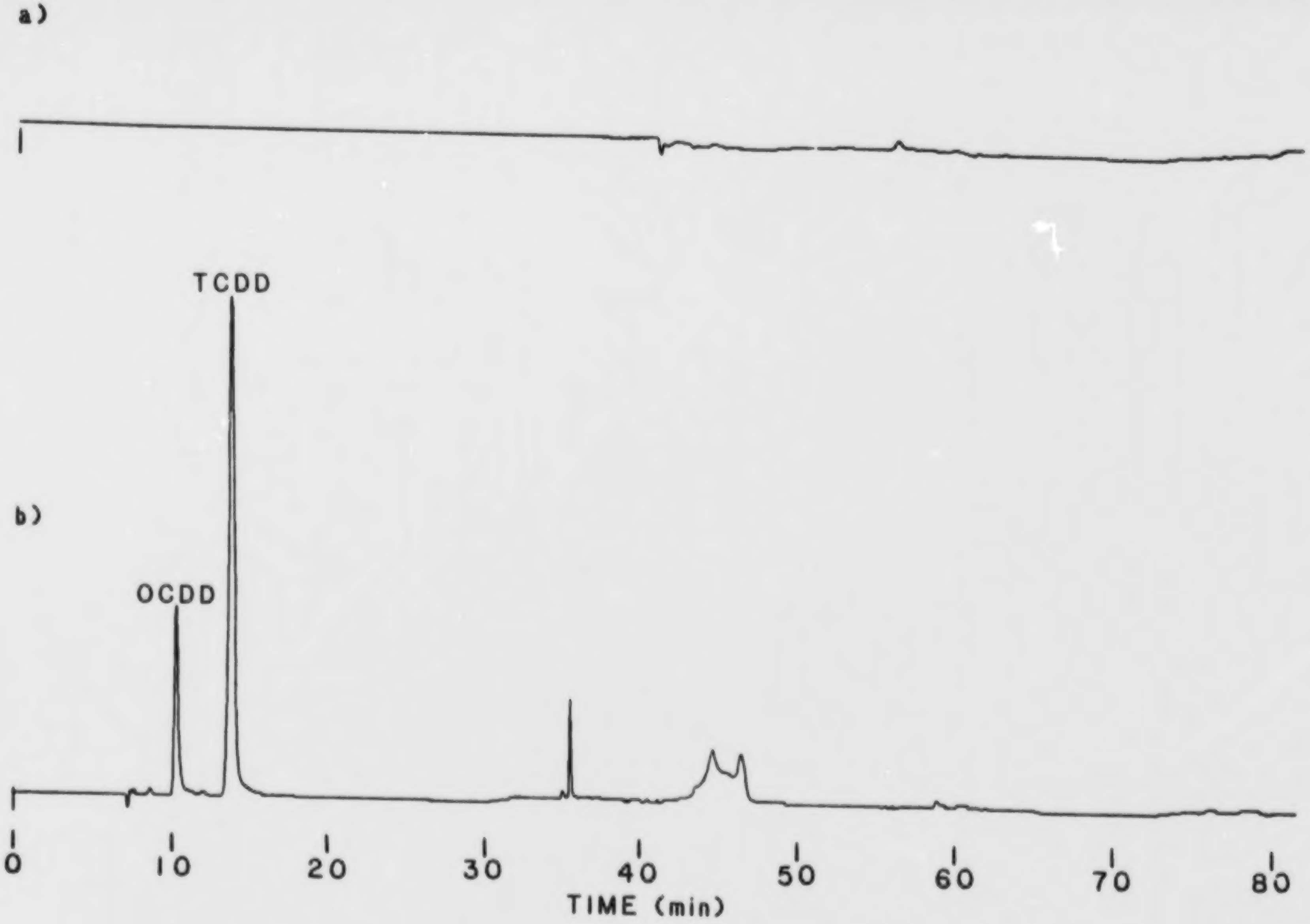

FIGURE 5: Normal phase HPLC traces (UV detection) for a) solvent blank and b) 1,2,3,4-TCDD and OCDD.

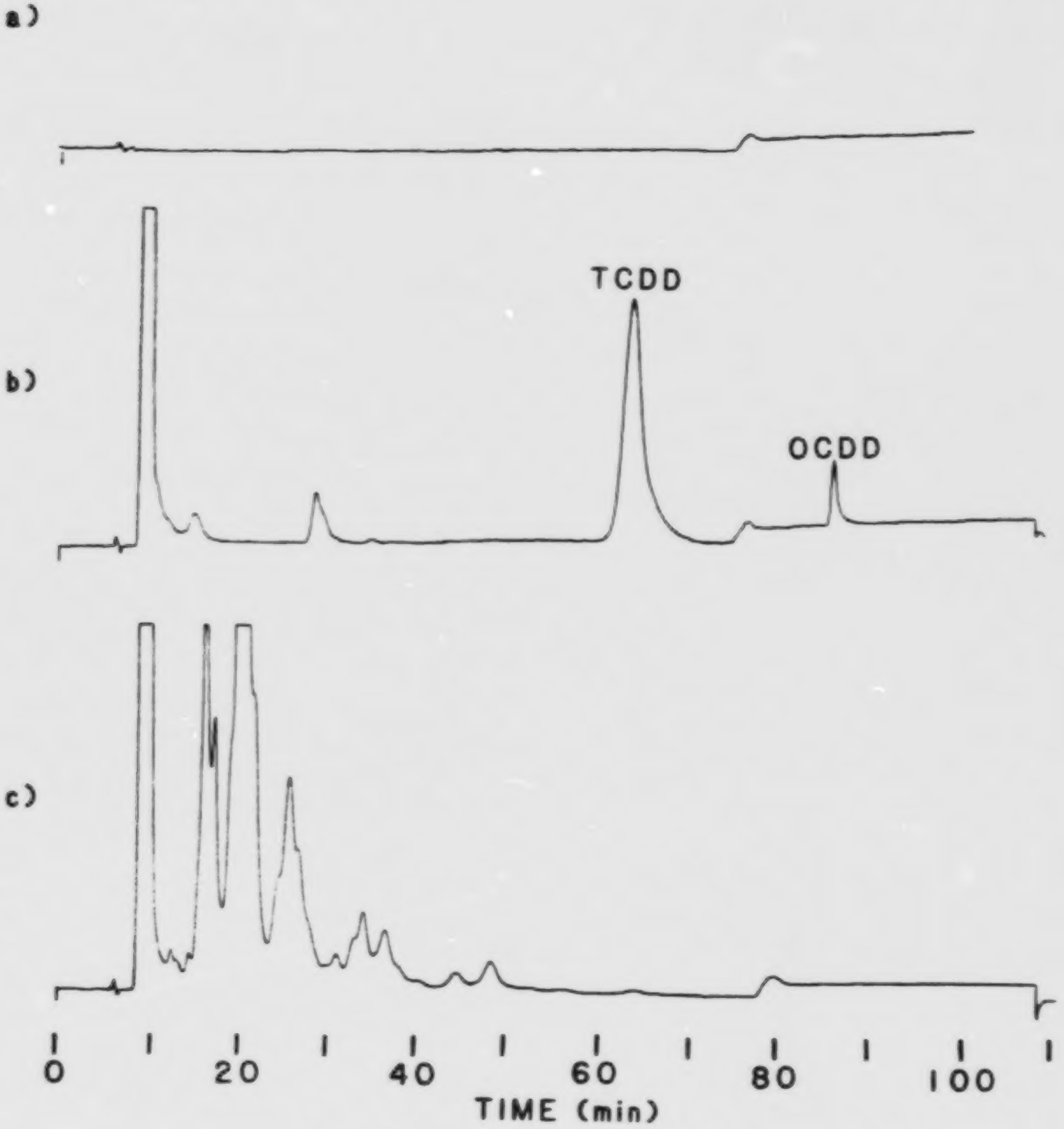

FIGURE 6: Reverse phase HPLC traces for a) solvent blank, b) 1,2,3,4-TCDD and OCDD, and c) PCB mixture (Aroclors 1016, 1242, 1254, and 1260).

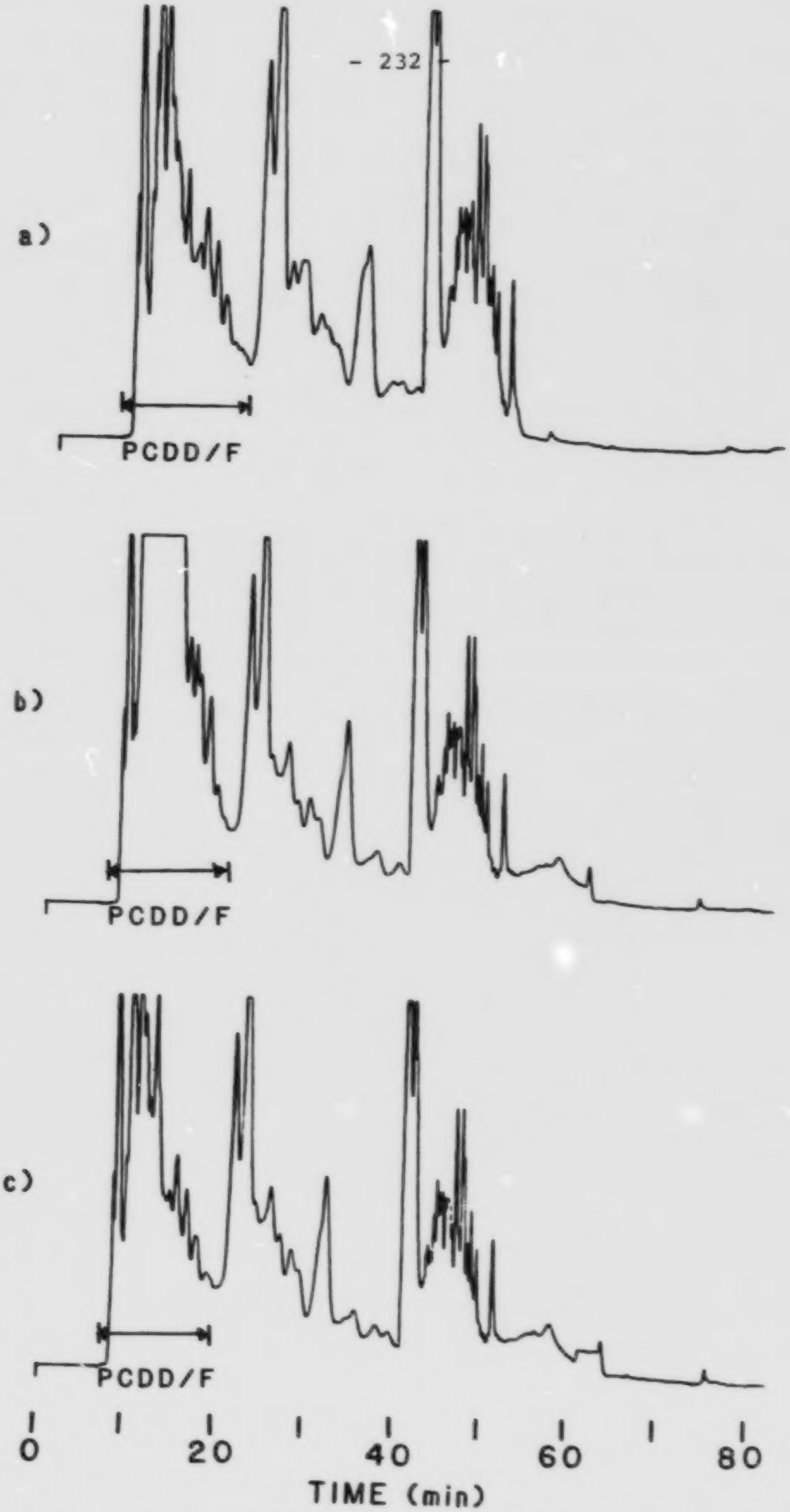

FIGURE 7: Normal phase HPLC traces (UV detection) of a) flyash extract, b) flyash extract fortified with PCB, and c) flyash extract fortified with fish tissue extract.

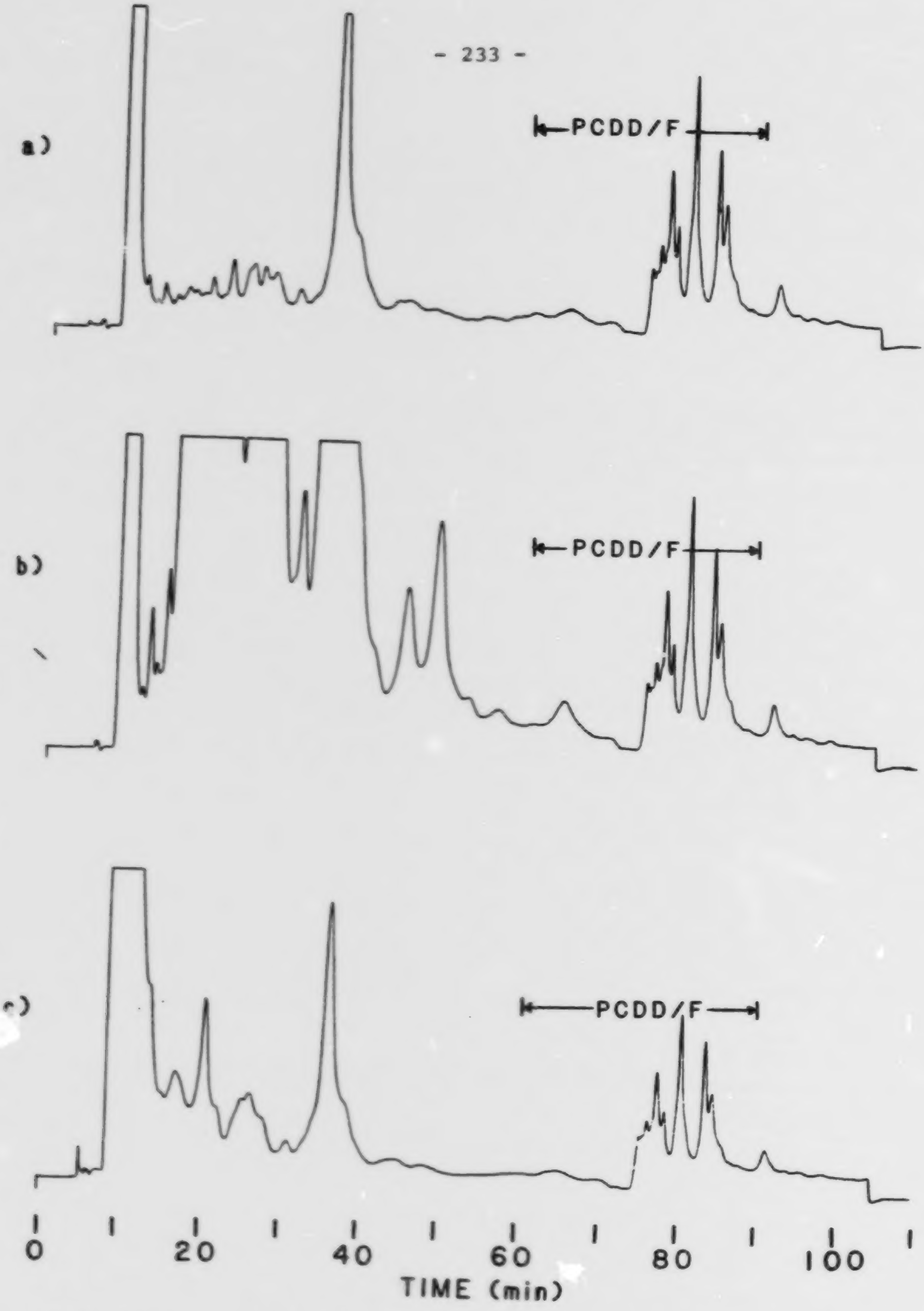

FIGURE 8: HPLC traces (UV detection) for the second-step fractionation of a) flyash extract, b) flyash extract fortified with PCB, and c) flyash extract fortified with fish tissue extract.

DEVELOPMENT OF A COST EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS OF TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGES AND FINAL EFFLUENTS

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ONTARIO MINISTRY OF THE ENVIRONMENT

INTRODUCTION

The development of analytical methods for efficient processing of wastewater sample has always been a continual challenge. The vast array of organics present at low concentrations in municipal wastewater requires complicated extraction, isolation and detection procedures. Added to this is the fact that large amounts of interferences are usually present in the extracts, consequently requiring extensive cleanup procedures.

In 1979, the US EPA published a series of procedures for the analysis of the 129 priority pollutants in wastewater(4). These procedures include (a) 12 methods for gas-liquid and high performance liquid chromatography with specific detectors and (b) 3 methods using gas chromatography/mass spectrometry for multiple measurements. Because of the high complexity of the organic contaminants in wastewaters, GC/MS methods are usually the methods of choice in most analyses. For example, Method 625 is a general screening method for extractable priority pollutants. This method, while very useful for most applications, has several shortcomings such as: 1) the initial base/neutral extraction may cause significant reduced recoveries of phenol, 2-methyl phenol and 2,4-dimethylphenol; 2) the bases such as benzidines and other amines are difficult to chromatograph; 3) presence of fatty acids in wastewater usually results in very complex chromatograms; 4) two extractable fractions are obtained using this method, which usually require two GC/MS analyses.

Another approach was funded by the USEPA to modify and develop an analytical approach to enable the analysis of raw wastewater and sludge samples. Results of this study were detailed in a report submitted to the EPA by F.P. DeWalle and E.S.K. Chian(5). The analytical method used in this study involved an acid/neutral extraction followed by a base extraction. Due to the high concentrations of organic interferences in this type of samples, special separation and cleanup procedures such as gel permeation chromatograhy, florisil chromatography and cesium silicate chromatography were required to facilitate analysis for individual group of compounds. This method produced a base fraction, 3 neutral fractions and 1 acid fraction which was derivatized with diazomethane.

The results of this study indicate detection limits of about 1 ug/L for the extractable organics and 5-10 ug/L in sludge samples. Although this method offers cleaner fractions for processing, there are several drawbacks that discourage its use for routine monitoring. Firstly, the procedure is time consuming and labor intensive, and consequently reduces sample throughput. Secondly, the multi-fraction approach results in more losses of organics due to the separation processes. Thirdly, the cost of analysis will be very high as it involves a minimum of three extractable fractions and one volatile fraction.

Since MOE has proposed a regulatory and compliance program which will require municipal STP's to begin monitoring for the presence of hazardous contaminants in thier raw sewage and final effluent, cost-effective analytical methodology is needed. The objective of this study is therefore to develop a reliable protocol which will maximize sample throughput and provides the required accuracy, sensitivity and precision for such analysis. To achieve the project objectives, two novel approaches have been investigated in this study : a) simultaneous in-situ acetylation and extraction coupled with the purge and trap method and b) dynamic thermal stripping method. Although the latter method showed promising results for most of the compounds under investigation, the simultaneous extraction and acetylation method was the method of choice due to the ease of automation.

The Ontario Ministry of the Environment has preliminary identified more than 84 compounds for this study. Based on the frequency of occurrence and concentration levels of organics reported in the previous studies (1-3), a target list was generated to represent a broad spectrum of organics and used throughout the study to test the protocol. These target compounds are listed in Table 1.

TABLE 1. LIST OF TARGET ORGANICS

Halogenated Aliphatics

Chloroform
Dichlorobromomethane
Tetrachloroethylene
Trichloroethylene
1,1,1-Trichloroethane
Vinyl Chloride

Halogenated Aromatics

Chlorobenzene
Hexachlorobenzene
1,4-Dichlorobenzene
Aroclor 1254

Non-Halogenated Aromatics

Benzene
Benzo(a)pyrene
Chrysene
Dibenzo(a,h)anthracene
Naphthalene
Styrene

Miscellaneus

Dimethyl Disulphide
1,4-Dioxane

Pesticides

Diedrin
gamma-BHC
Diazinon
p,p'-DDT
Chlordane
Atrazine

Phenols

Phenol
Pentachlorophenol
o-Cresol
2,4,6-Trichlorophenol

Phthalate Esters

Bis(ethylhexyl)phthalate

Amines

Aniline

Ethers

Diethyl Ether

OVERALL APPROACH

The finalized approach used for the determination of the target organic pollutants in the reagent water, raw sewage and final effluent involved the addition of methylene chloride, potassium bicarbonate and acetic anhydride to the water sample. The sample was then extracted for 15 minutes and the the organic phase collected. Under the basic pH, the neutral and basic compounds were extracted into the methylene chloride layer. The phenolic compounds were converted by acetic anhydride to their respective acetates and the amines to their corresponding amides. These derivatized products were then extracted into the methylene chloride layer. Since the acids themselves were not derivatized by the acetic anhydride, they remained in the aqueous layer.

Using this method, all bases, neutrals and phenols can be extracted in one fraction , the overall recoveries of phenolics will greatly be increased because of the single extraction. Quantitation of the amines is better due to better peak shape. Since free fatty acids are known to be a major class of interferences in wastewater, using this method, they will stay in the aqueous layer, hence producing a cleaner extract for chromatographic analysis.

The compounds of concern were analysed without further cleanup by GC/MS using high resolution capillary column and selected ion monitoring mode. Quantition of the derivatized compounds were achieved using the labelled standards spiked into the sample and analyzed under the same conditions. The rest of the underivatized compounds were based on the internal standard quantitation. Relative response factors obtained from the standard solutions were used as correction factors in the calculation of the organic concentrations. This analytical method provides high sensitivity, high resolution of target organics from the background interferences and high selectivity of the detector responses.

The volatile organic fraction was analysed using the purge and trap method by GC/MS using capillary column in the full scan mode. A 30 ml aliquot of the water sample is used for analysis.

A total of two fractions, a volatile and a semivolatile fraction, were obtained from each sample using this protocol. This approach eliminates the cleanup steps for the semivolatile fraction, improves the recovery of the phenolic compounds, provides better detection of the amines and substantially increase sample throughput.

EXPERIMENTAL

SIMULTANEOUS IN-SITU ACETYLATION AND EXTRACTION

All raw sewage and final effluent samples were collected from Main Treatment Plant in Toronto and provided by the Water Resources Branch of the Ministry of the Environment. A 500 ml sample of wastewater was accurately measured and fortified with several labelled compounds to monitor the extraction efficiency.

A 50 ml aliquot of methylene chloride and a surrogate mixture of phenols were added to the water sample in an erlenmeyer flask and mixed thoroughly for 10 minutes on a magnetic stirrer. Approximate 10g of anhydrous $KHCO_3$ was then added and stirred for another 5 minutes to ensure complete dissolution of the solid. An accurately measured 2.5 ml of acetic anhydride was finally added to the flask and vigorously stirred for 15 minutes. At the end of the extraction, the two phases were allowed to separate in a separatory funnel and the organic layer collected in a round bottom flask. When necessary, the samples were subjected to centrifugation to break the emulsions. The extractive acetylation was repeated twice with 50 ml of CH_2CL_2 and 15 minutes of stirring each time. The methylene chloride layers were then combined, passed through pre-washed sodium sulfate, and concentrated to about 2-3 ml. The extract was further concentrated to 1 ml with a gentle stream of nitrogen and spiked with an internal standard prior to autosampler processing.

INSTRUMENTATION

Analysis of the extractable organics was performed on a Hewlett Packard Mass Selective Detector system interfaced with a HP 5890 gas chromatograph. Chromatographic separation was achieved with a J & W DB-5 fused silica capillary column (30 m x 0.25mm, 0.25um film thickness). The chromatographic conditions were as follows: Injector temperature, 250°C; temperature program,70°C hold for 1 min, 20°C/min to 170°C , 5°C/min to 200°C, 20°C/min to 280°C with a final hold of 12 minutes. The interface temperature was 285°C. The linear velocity of the helium carrier gas was 30 cm/sec. Samples were introduced in the splitless mode with the solvent vent closed for 0.5 min after injection.

Mass detector conditions were as follows: electron energy, 70eV; MS operating mode, SIM; Dwell time per ion, 50 msec. Electron impact spectral data was acquired and processed by the HP 9816 computer and the corresponding MSD software.

Volatile organics and the sorbent tube samples were analysed on a UNACON 810B automatic concentrator (Envirochem Inc.). This instrument was equipped with a sparging assembly for analysis of volatile organics in water, and a desorber unit for thermal desorption of the sorbent tubes. The internal trapping system consisted of a large bore primary trap which permitted preliminary separation of compounds of interest from the carrier gas. The secondary small bore trap was approximately one-tenth the capacity of the first trap and allowed for an efficient transfer of the retained compounds to the capillary column.

Initial concentrator operating conditions were: transfer line to MS, 280°C; valve compartment, 250°c; trap 1 desorbed at 300°C with a helium flow of 50ml/min for 5 minutes; trap 2 desorbed at 300°C with a helium flow of 3 ml/min for 5 minutes onto a 30 m DB-5 column.

For volatile organics, a 30 ml aliquot of the water sample was transferred to a 50 ml sparging vial and purged for 15 minutes at a flow rate of 50 ml/min at 50°C. For sorbent tube analysis, the tube was placed inside a desorber unit with both ends tightly sealed by vespel/graphite ferrules. The sorbent tube was then rapidly heated to 300°C with a helium flow of 50 ml/min for 15 minutes to release the organics into the first trap. By sequential heating of the first and second trap, a discrete narrow-band plug of sample was deposited on the head of the column.

RESULTS AND DISCUSSION

EXRACTION METHOD

Recoveries of target organics using the in-situ acetylation and extraction technique have been conducted in final effluent, raw sewage and reagent water matrices. Results of these analyses are presented in Tables I to III.

Initial extraction using 500 ml of organic free water indicates good recoveries for phenolic compounds which range from 80% for pentachlorophenol to 94% for o-cresol. These recoveries are far better than those of EPA method 625 due to the fact that the phenols were extracted and derivatized in the same

TABLE 1

RECOVERIES OF THE TARGET ORGANICS IN REAGENT WATER

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	8.82	10.7	86.0
Aniline(A)	15.00	14.06	9.7	93.7
O-Cresol(A)	10.58	12.09	8.8	94.9
Napthalene	10.18	9.31	15.4	91.5
2,4,6 TCP(A)	9.94	9.12	5.5	91.7
HCB	10.10	9.03	5.4	89.4
Atrazine	11.26	10.76	2.5	95.6
Gamma-BHC	17.00	17.80	2.9	104.7
Diazinon	21.50	19.31	4.4	89.8
Pentachlorophenol(A)	9.94	7.93	9.7	79.8
Alpha-Chlordane	12.70	11.82	8.0	93.1
Dieldrin	10.12	9.37	5.4	92.6
4,4'-DDT	10.06	9.37	3.8	96.7
Chrysene	22.50	21.94	8.5	97.5
Bis(Ethyl-Hexyl)Phthalate	10.32	7.63	6.0	74.0
Benzo(A)Pyrene	10.20	8.98	7.1	88.0
Dibenzo(A,H)Anthracene	21.20	19.52	6.1	92.1

(A) = Acetylated

TABLE II

RECOVERIES OF THE TARGET ORGANICS IN FINAL EFFLUENT

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	7.75	7.2	75.5
Aniline(A)	15.00	14.42	13.5	96.1
O-Cresol(A)	10.56	11.07	24.5	104.6
Napthalene	10.16	9.03	7.6	91.0
2,4,6 TCP(A)	9.94	8.47	4.4	91.0
HCB	10.10	9.60	3.7	95.0
Atrazine	11.26	9.20	9.8	81.7
Gamma-BHC	17.00	16.28	5.2	95.8
Diazinon	21.50	18.14	7.2	84.4
Pentachlorophenol(A)	9.94	8.58	4.3	88.3
Alpha-Chlordane	12.70	9.16	4.5	72.1
Dieldrin	10.12	8.69	3.5	85.8
4,4'-DDT	10.06	11.43	16.17	94.4
Chrysene	22.50	16.41	2.2	72.9
Bis(Ethyl-Hexyl)Phthalate	10.32	7.76	12.9	75.7
Benzo(A)Pyrene	10.20	9.43	6.5	92.5
Dibenzo(A,H)Anthracene	21.20	20.41	7.5	96.3

(A) = Acetylated

TABLE III

RECOVERIES OF THE TARGET ORGANICS IN RAW SEWAGE

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	7.52	6.0	73.3
Aniline(A)	15.00	13.39	6.1	89.3
O-Cresol(A)	10.58	7.66	9.6	72.4
Napthalene	10.18	8.92	6.5	87.6
2,4,6 TCP(A)	9.94	9.09	2.7	91.4
HCB	10.10	10.80	2.8	106.9
Atrazine	11.26	11.18	17.1	99.3
Gamma-BHC	17.00	13.85	9.1	81.5
Diazinon	21.50	22.28	3.6	103.6
Pentachlorophenol(A)	9.94	8.73	9.8	87.8
Alpha-Chlordane	12.70	10.20	9.9	80.3
Dieldrin	10.12	6.92	6.0	68.4
4,4'-DDT	10.06	7.98	7.9	79.3
Chrysene	22.50	16.86	7.0	74.9
Bis(Ethyl-Hexyl)Phthalate	10.32	10.68	14.2	103.5
Benzo(A)Pyrene	10.20	10.31	11.3	101.0
Dibenzo(A,H)Anthracene	21.20	19.30	4.6	91.0

(A) = Acetylated

fraction, thus eliminating losses in the initial base/neutral fraction. In addition to the phenols, amines such as aniline were also converted to amides which greatly improved the chromatography and ultimately the sensitivity.

The recoveries of the phenols were calculated based on those obtained from the repective standards under the same conditions as detailed in the experimental section. The quality of the data will not be affected since both standards and samples were treated the same.

It is well known in the EPA method 625 that some organochlorine pesticides such as alpha and beta BHC, endosulfan I and II and endrin are subject to decomposition under the alkaline conditions of the extraction step. By using this in-situ acetylation method in which a weaker base such as potassium bicarbonate was used, the recoveries and reproducibility of these compounds were found to improve significantly.

Experiments were also carried out to determine the recoveries of the EPA priority pollutants using this procedure. Results indicate that the benzidine and 3,3'-dichlorobenzidine were acetylated. Good recoveries of most of the EPA compounds including N-nitroso-di-n-propylamine, N-nitroso-dihenylamine, diphenyl hydrazine and isophorone. Among all the EPA compounds, 4,6 dinitrophenol and 2,4 dinitrophenol were found to have low recoveries. Further work will be conducted to investigate this problem.

The isolation and identification of trace hazardous organics from complex background is the prime aim of any wastewater extraction procedure. In most methods used today, gel permeation chromatography or other column cleanup procedures are frequently employed to reduce interferences, thus resulting longer sample processing time. Using this in-situ acetylation method, the fatty acids which are present at high concentrations in municipal wastewater would not be derivatized and hence remain in the aqueous layer. This greatly reduces the chromatographic background and eliminates the need for a cleanup step. On the other hand, by eliminating the acid compounds, the phenoxy herbicides which contain the carboxylic acid functional group would not be detected.

Using this approach, all bases, neutrals and phenols will be extracted in the same fraction. Hence, only one extractable and one volatile fraction are needed for each sample. With autosamplers for sample introduction, coupled with extensive software development for data processing, a high sample throughput with minimum manpower requirement can be achieved.

VOLATILE ORGANIC ANALYSIS

In combination with the in-situ acetylation method, a capillary purge and trap method was used for the analysis of the volatile organics. Depending on the sample volume, this technique can be used to produce sub-ppb detection limits for a large number of volatile compounds.

Table IV Mean % Recoveries of Volatile Organics Using Purge and Trap Method

Compound	Mean Recovery (%)	C.V. (%)
Vinyl Chloride	93.9	10.3
Chlorofrom	81.2	3.6
1,1,1-Trichloroethane	102.5	9.5
Benzene	91.4	7.2
Bromodichloroethane	96.0	4.9
Trichloroethylene	91.1	7.4
Tetrachloroethylene	80.3	7.6
Chlorobenzene	78.5	5.4
Diethyl Ether	66.4	9.7
Dimethyl Disulphide	80.0	7.9
Styrene	91.1	9.2
1,4-Dioxane	0.3	8.5

The purging efficiency and reproducibility of the target compounds are depicted in Table IV. The purging efficiency is a reflection of the percentage of the amount of a specific compound that can be recovered from water. In these analyses, the accuracy of the results was not affected by the recoveries since samples and standards were analysed using the same procedures.

In this study, it was observed that the recovery of 1,4-dioxane was extremely poor. This was mainly due to the misicibility of this compound with water. With an increase in temperature during sparging and a higher ratio of gas flow verus sample size, a better recovery was obtained. Recoveries of the other volatile compounds were very good. They ranged from 66% for diethyl ether to 102% for 1,1,1-Trichloroethane. The coefficients of variation for majority of the compounds were well within 10%.

DETECTION SYSTEM

In this project, a Hewlett Packard mass selective detector was used. Customized software was developed to allow unattended sample handling and data processing.

This detector was exclusively used in the "Selected Ion Monitoring" mode to obtain the best possible sensitivity, improved quantitation and increase computer storage capability. The sensitivity of the SIM mode (10-100pg) was sufficient to detect concentrations of organics found in raw sewage or final effluent.The readily detectable limits of 100 pg for most of the hazardous organics enabled only 500 ml of sample to be routinely processed.

For each parameter in the target list, three ions were selected based on their intensity and uniqueness. To confirm the identity, retention times and the ratio of the two qualifying ions to the quantition ion had to be within the strictest tolerence. Two time reference peaks were chosen to help define the relative time window for each parameter. Internal standard quantitation method was used in these analyses.

For Aroclor 1254, a quantitation ion was selected from each of trichloro, tetrachloro, pentachloro and hexachloro cogener groups, these, coupled with the two qualifying ions and scanning over the entire range of the expected retention times, provided positive confirmation of the presence of Aroclor 1254. Quantition was achieved by the summation of these target peaks.

SOFTWARE APPROACH

Automation is becoming an important aspect in most analytical chemistry laboratories. There are obvious reasons for increasing automation such as : less time is spent in sample introduction and repetitive laboratory endeavour; greater standardization of data collection and reduction operations results; more attention is paid to problem solving; and flexibility is increased.

In order to assure the accuracy of the detection and maximum efficiency for sample processing and interpretation, extensive software development was required. Our major objective in this regard was to effectively identify and quantify the compounds of interest under various adverse chromatographic conditions such as background interference, overloading and saturation problems which commonly occur in this type of analysis.

Software development from these concerns resulted in the creation of a series of independent programs. These programs were developed to ease the process of data reduction and achieve a high level of automaticity. Furthermore, they can either be linked together or processed individually. Typical examples of some of the programs are:

* a program to extract and integrate ions of interest and to display the information in a way which is easily witnessed by the operator (Figure 3)
* a program to detect the overloading and saturated peaks
* a program to provide spectra of each peak in the chromatgram

- a program to automatically initiate and set up an autosequencing method
- the "Mann Link", a top view type program that adds a new dimension to autosequencing capability and flexibility
- a full and sophisticated background substracted spectra library search program
- a program that allows a visual pattern recognition format for Aroclor 1254 (Figure 6)
- a program to conduct daily QA/QC and compare previous results automatically

Following each acquisition, data reduction macros were used to display the three ions for each compound, and to monitor the quality of the integration. Separate tests were automatically run to flag any saturated or overloading peaks. Subsequent internal standard reports were processed and automatically printed.

Peak identification in the report program had to meet the following criteria:

i) the strict adherence to the correct relative retention time window with respect to the two time reference peaks

ii) the presence of the designated quantitation ion and two qualifying ions

iii) the correct ion ratios of the two qualifiers to the quantition ion

iv) the peak area of the internal standard must be within a specific tolerence

Following these acquisitions and reports, further data reduction macros were automatically envoked to display ions and qualifiers for Aroclor 1254. Special programming displayed Aroclor 1254 in such a way as to allow visual pattern recognition by the operator similar to that being done with the electron capture detector. Several options then followed: library search for a number of peaks or every peak in the chromatogram; display spectra of every peak; continue injection of the same batch of samples or process another batch using different macros; transfer the data to another media and delete the file on hard disk.

In every aspect these types of software development are to allow complete flexibility and to achieve maximum sample throughput .

ACKNOWLEDGEMENTS

The authors are grateful to the Ontario Ministry of the Environment for financial support and would like to thank the Water Resources Branch of the MOE and the Toronto Main Treatment Plant for providing the raw sewage and final effluent samples.

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APPLICATION OF GAS CHROMATOGRAPHY WITH HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTES

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Introduction

The helium microwave plasma, particularly at atmospheric pressure using a Beenakker TM_{010} cavity, shows a great deal of promise as a gas chromatographic detector because of its ability to detect a very wide range of elements, both metal and non-metal[1,2]. By incorporating a polychromator as a part of the instrument, one can derive the benefits of simultaneous, multi-element detection such as higher speed of analysis and smaller sample requirements. This paper describes a helium microwave plasma detector for GC that was developed by the authors.

Experimental

Figure 1 shows a block diagram of the entire instrument. Helium, after being purified, goes into the GC and the gas control unit. This provides for solvent venting as well as supplying helium plasma support flow. Independent of the column flow, scavenging or doping gases can also be introduced through this unit. A scavenger is a gas such as nitrogen or oxygen that when introduced into the plasma at low concentrations removes carbon deposits on the torch walls. There is also the capability of introducing a doping gas. Some workers[2] have seen improved sensitivities for a number of elements by doping the plasma with a small flow of hydrogen. The GC-plasma interface incorporates fluidic logic switching. The solvent is vented so that it does not disrupt the plasma. Subsequent GC eluent reaches the plasma without having to pass through valves. A 200 watt microwave generator is linked to the Beenakker cavity. A nine channel polychromator was built to provide simultaneous detection. It has chart recorder outputs and also a socket for direct connection to a Spectra-Physics SP 4000 computer. The interface oven and Beenakker cavity are rigidly mounted together on a common support. This support is on an X, Y, Z stage which allows precise and reproducible positioning of the Beenakker cavity in front of the entrance optics to the spectrometer. The interface oven consists essentially of a heated aluminum block containing a manifold which has two side arms.

Figure 2 shows the optical layout of the multi-channel spectrometer. Light from the plasma is focused by a lens onto the dual entrance slits. The two entrance slits allow square wave wavelength modulation for background correction. A chopper wheel lets light alternately through one slit or the other. On the far side of the Rowland circle is a concave holographic grating having 1180 lines per millimetre. The light is dispersed by the grating across the Rowland circle to the nine exit slits located on the bridge on the far side.

Behind each slit is a mirror at 45° which reflects the light up to the end-on photomultiplier tube for that element located on top of the bridge. There is an order sorting filter in front of each PMT.

The multichannel spectrometer was aligned to look at the following nine elements: carbon, phosphorus, mercury, bromine, chlorine, sulfur, fluorine, nitrogen, and oxygen. Background correction for each analytical line was accomplished by monitoring the intensity at the peak wavelength and subtracting from it the intensity 1.0 nm away from the peak. A synchronous detector circuit was incorporated into the electronics of each channel to provide this function.

One of the problems many researchers have seen is the very large background levels of nitrogen and oxygen. This was observed in this work as well. Oxygen exists as an impurity in the helium gas supply, it can come from column bleed, it can come from etching of the quartz torch and it can also enter the plasma by back diffusion from the open end of the torch. Nitrogen can arise from the first and fourth of these sources as well.

Because it was thought that back diffusion from the open end of the torch might be a significant source of nitrogen and oxygen, a flush cell was devised to be attached to the end of the discharge tube. One end of the flush cell was connected to the discharge tube with a straight Swage union. Additional helium was forced in through a sidearm. All of the helium exhausts through another sidearm and through a length of aluminum tubing. It was hoped that the length of the path for back diffusion was great enough to minimize back diffusion significantly. The levels of oxygen and nitrogen were seen to go down when the flush cell was used. Unfortunately, the reductions were not enough to allow reliable detection of nitrogen-and oxygen-bearing compounds in chromatographic eluents.

Results

Experiments were carried out to determine the dynamic range of each channel. For these experiments, the response of each signal channel was integrated to compensate for changes in peak shape as a function of the amount of material eluting in the column eluent. Various concentrations of the test compounds were used, up to a maximum of 5%. Calibration curves were constructed by plotting the response as integrated area versus amount of each element injected on logarithmic scales. A typical calibration curve is the one for sulfur using dibutylsulfide, shown in Figure 3.

In general, the linear dynamic range of each channel extends up to approximately 50 ng of each element. Under the conditions used for these determinations, the peak width varied between 2 and 3 seconds for each compound. Since the detection limits for the elements in general are between 10 and 20 pg/sec, the absolute detection limit for most of the elements is approximately 50 pg. Thus the linear dynamic range for the elements determined is approximately 1,000.

One of the most important things to determine was the position of maximum intensity for the different elements within the plasma torch. A part of this was the determination of how the position of maximum intensity changed as a function of helium flow rate and applied power. Profiling studies of element emission intensity across the torch were done by moving the Beenakker cavity with respect to the spectrometer. Figure 4 shows the carbon emission intensity across the torch with the helium flow ranging from 42 to 210 mL/min. The maximum intensity was in the centre of the torch and changing the helium flow did not change the position of the maximum intensity. This was observed for all of the elements studied.

Profiles were also done across the torch while varying the applied power. Figure 5 shows such a profile for phosphorus. Again, the position of maximum intensity is at the centre and it does not vary with incident power. The general conclusion that can be drawn from the profiling studies was that all the elements had their maximum intensity at the centre of the torch and that varying power or helium flow did not change the position of maximum intensity. This was an important result because it meant that when these parameters are varied it is not necessary to reposition the cavity with respect the spectrometer for maximum sensitivity.

Figure 6 shows the intensity of the chlorine signal as a function of incident power. Increasing the power increases the signal intensity and this is typical of the elements that were studied.

The signal intensity was also monitored while varying the helium flow rate. Figure 7 shows the results for carbon. Again, this is typical of the other elements. Reducing the helium flow would increase the emission intensity, probably, because at a lower helium flow the analyte has a longer residence time in the plasma.

Based on the studies of emission intensity as a function of power and helium flow, a set of optimum conditions were established that would be the best overall for all of the elements. These compromise conditions are 85 watts of incident power and 50 mL/min of helium plasma flow. Using these conditions detection limits and selectivities against carbon were determined. These are shown in Table I.

Conclusions

The helium microwave plasma has demonstrated many desirable characteristics as a simultaneous multielement detector for gas chromatography. It has also been widely studied as a detector in non-chromatographic instrumentation. The plasma has been used to quantify such species as sulfur gases[3], carbonates in coal fly ash[4], heavy metal salts[5], tetraalkylleads[6], and volatile organo-mercury compounds[7].

Acknowledgement

This work was conducted with funding through the Department of Supply and Services under the auspices of the Canada Centre for Inland Waters.

TABLE 1

Detection Limits and Selectivities for Simultaneous Determination a)

Element	Detection Limit, pg/s	Selectivity vs. C b)
Br	27	180
C	4	1
Cl	12	200
F	11	366
Hg	1	131
P	4	1370
S	32	60

a) plasma operating conditions 85 watts incident power, 0-2 watts reflected power, 50 mL/min He plasma support flow rate.

b) using n-decane

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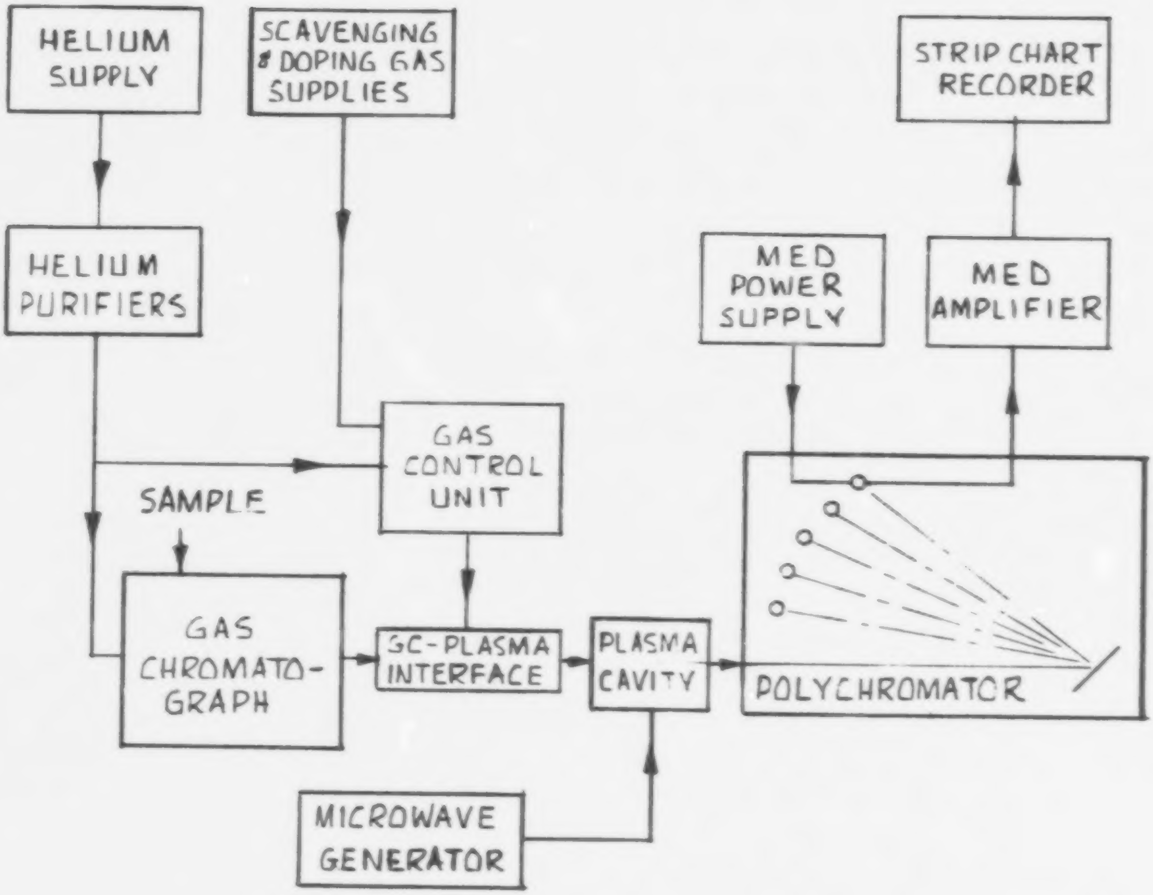
HELIUM SUPPLY
SCAVENGING & DOPING GAS SUPPLIES
STRIP CHART RECORDER
HELIUM PURIFIERS
MED POWER SUPPLY
MED AMPLIFIER
GAS CONTROL UNIT
SAMPLE
GAS CHROMATOGRAPH
GC-PLASMA INTERFACE
PLASMA CAVITY
POLYCHROMATOR
MICROWAVE GENERATOR

FIG. 1

BLOCK DIAGRAM OF THE MED 650

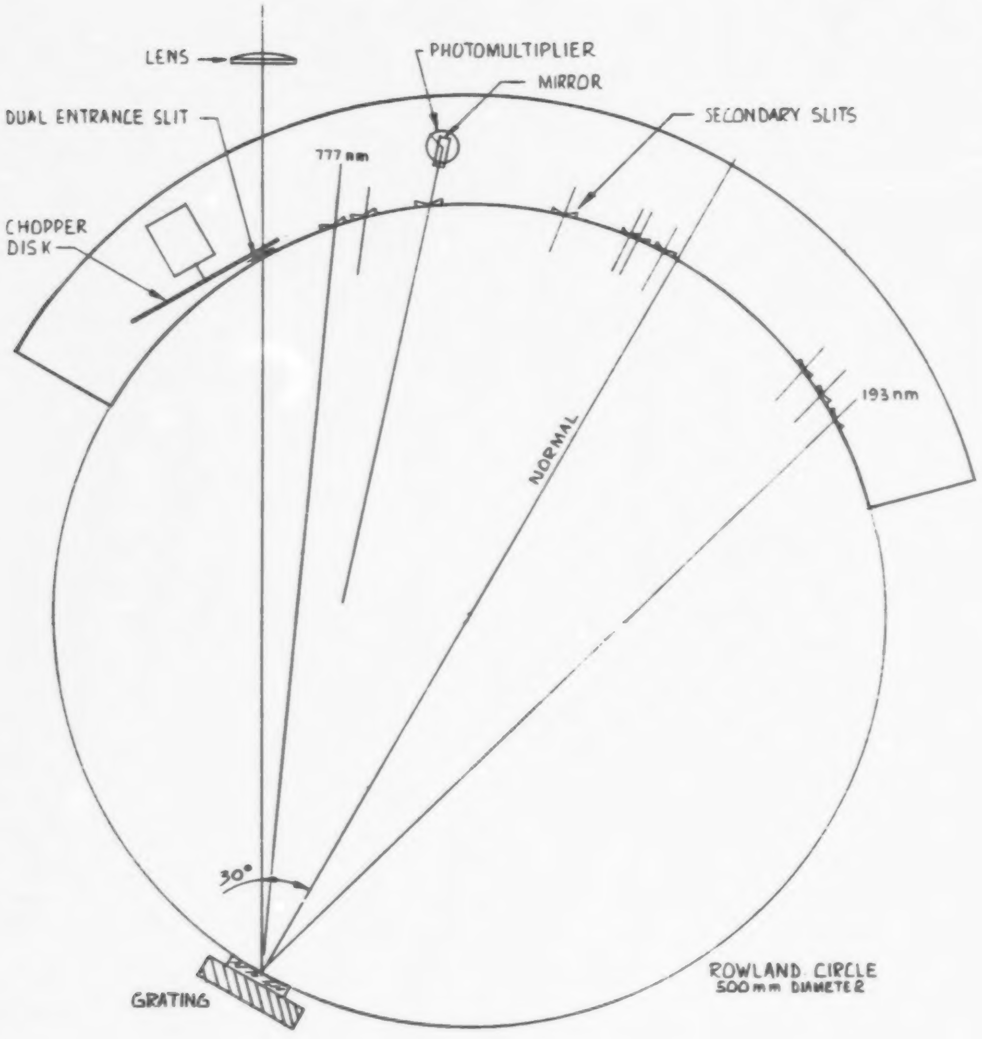
LENS
PHOTOMULTIPLIER
MIRROR
DUAL ENTRANCE SLIT
SECONDARY SLITS
777 nm
CHOPPER
DISK
193 nm
NORMAL
30°
GRATING
ROWLAND CIRCLE
500 mm DIAMETER

FIG. 2

OPTICAL LAYOUT OF MULTICHANNEL SPECTROMETER

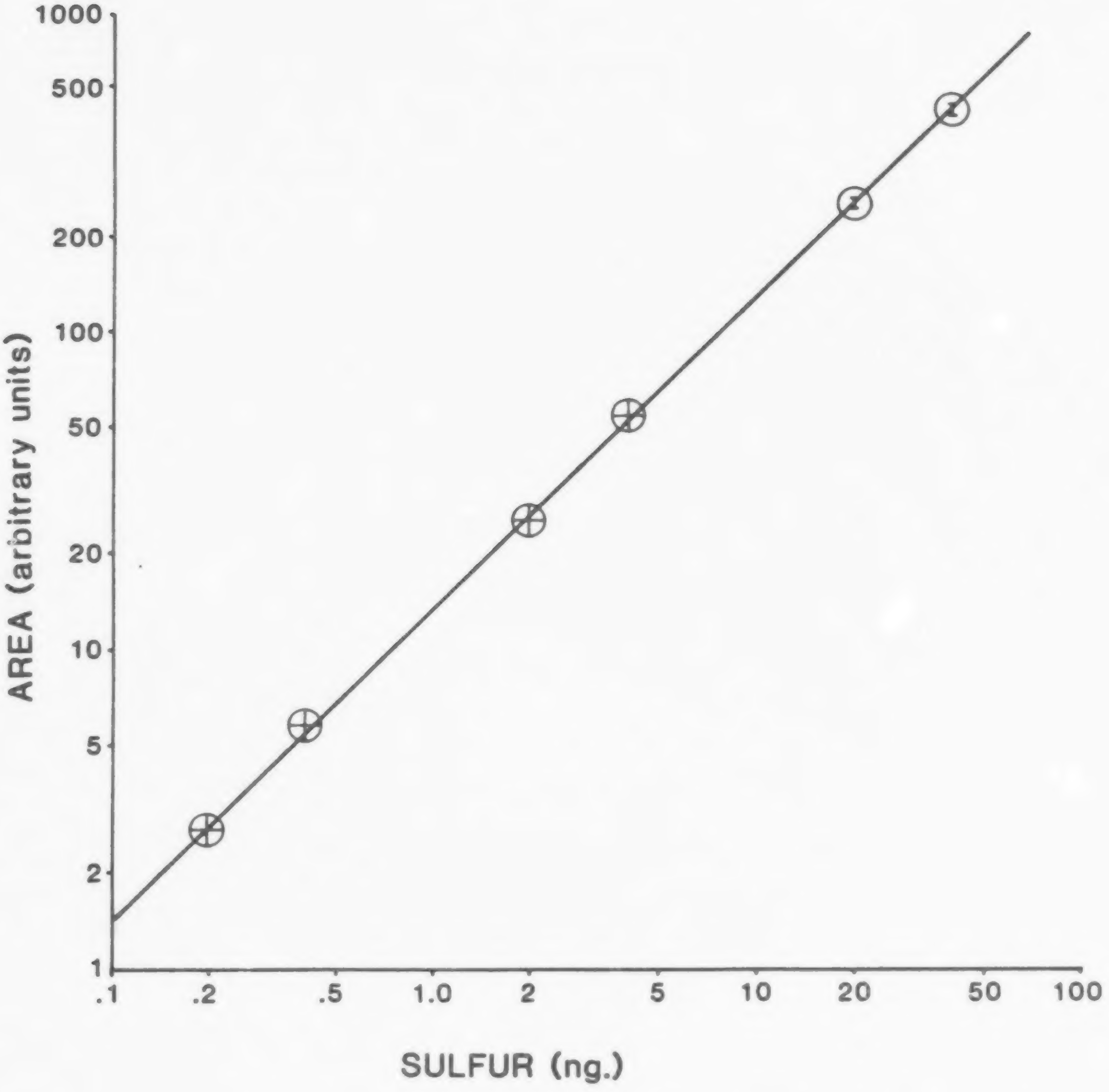

FIG. 3: Calibration Curve for Sulfur Using Dibutylsulfide

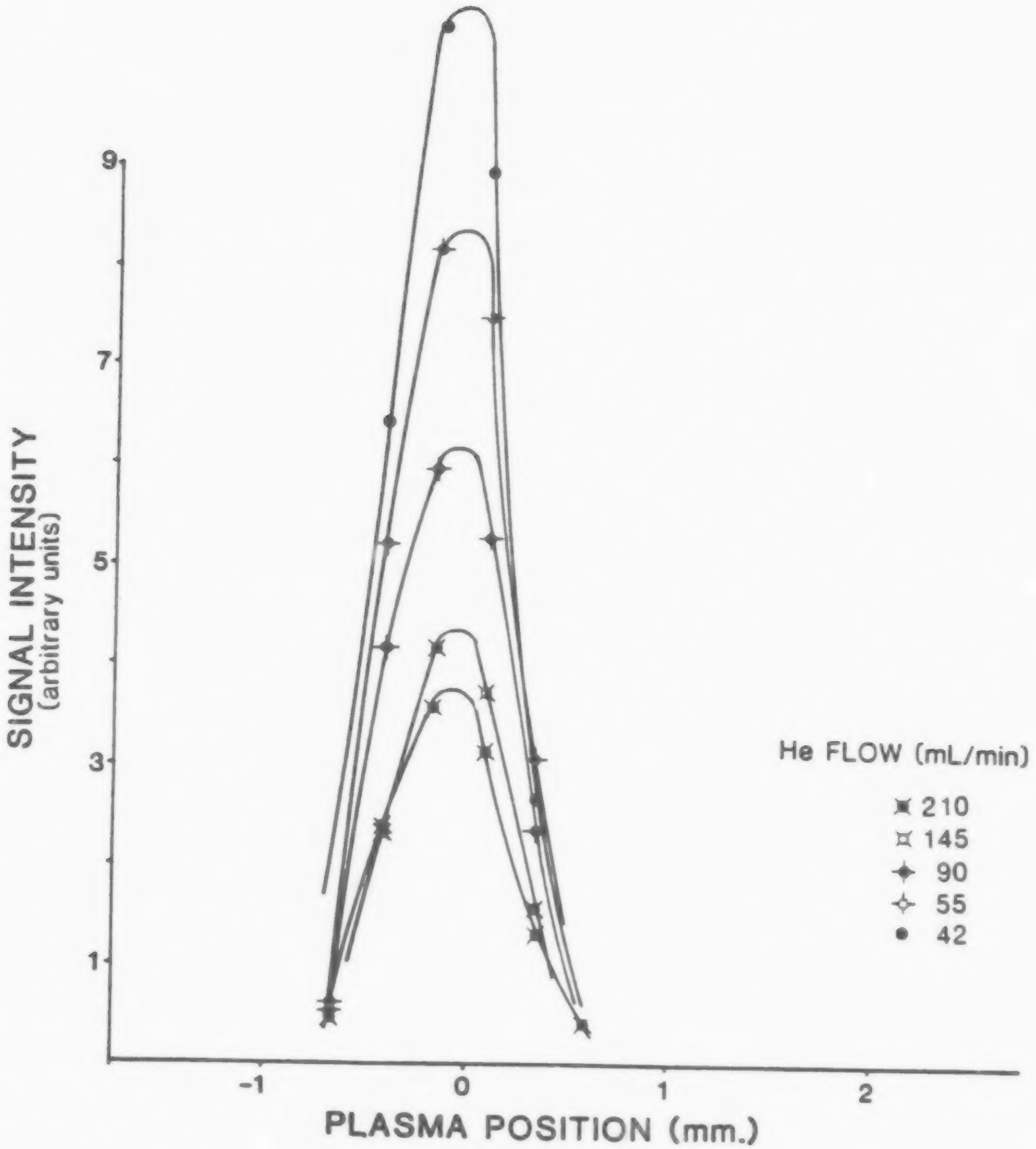

FIG. 4: Carbon Profile at Different Flows (85 Watts)

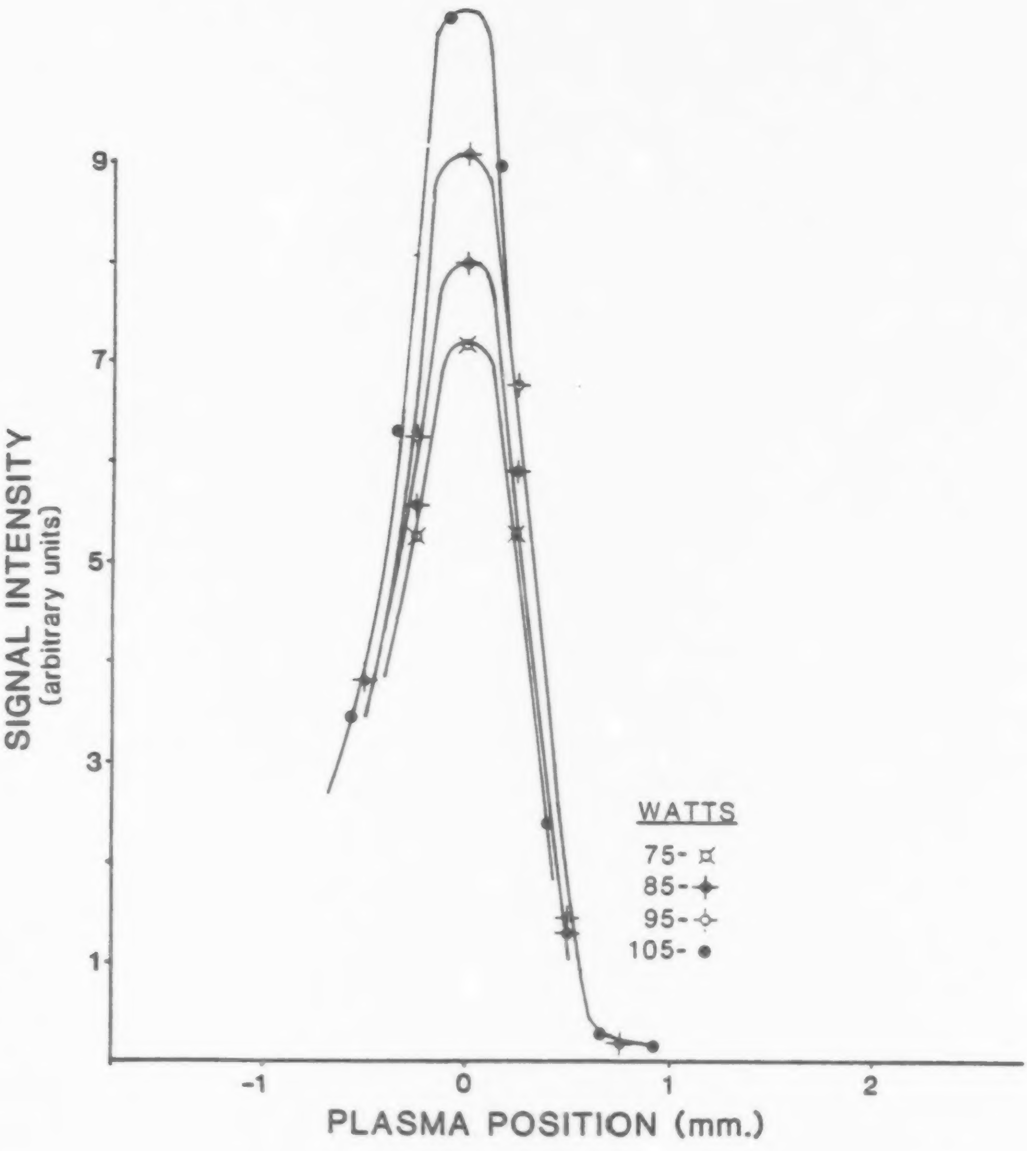

FIG. 5: Phosphorous Profile at Different Powers

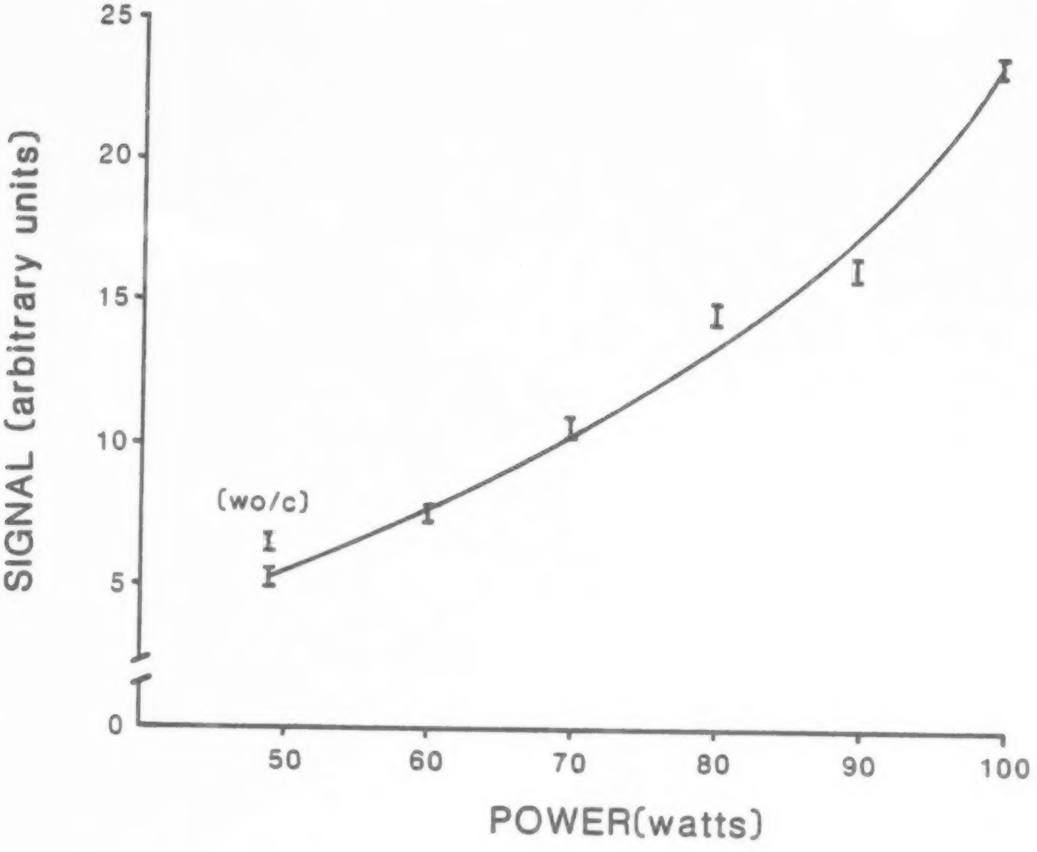

Figure 6

Chlorine Signal versus Incident Power; He plasma flow rate = 42 mL/min

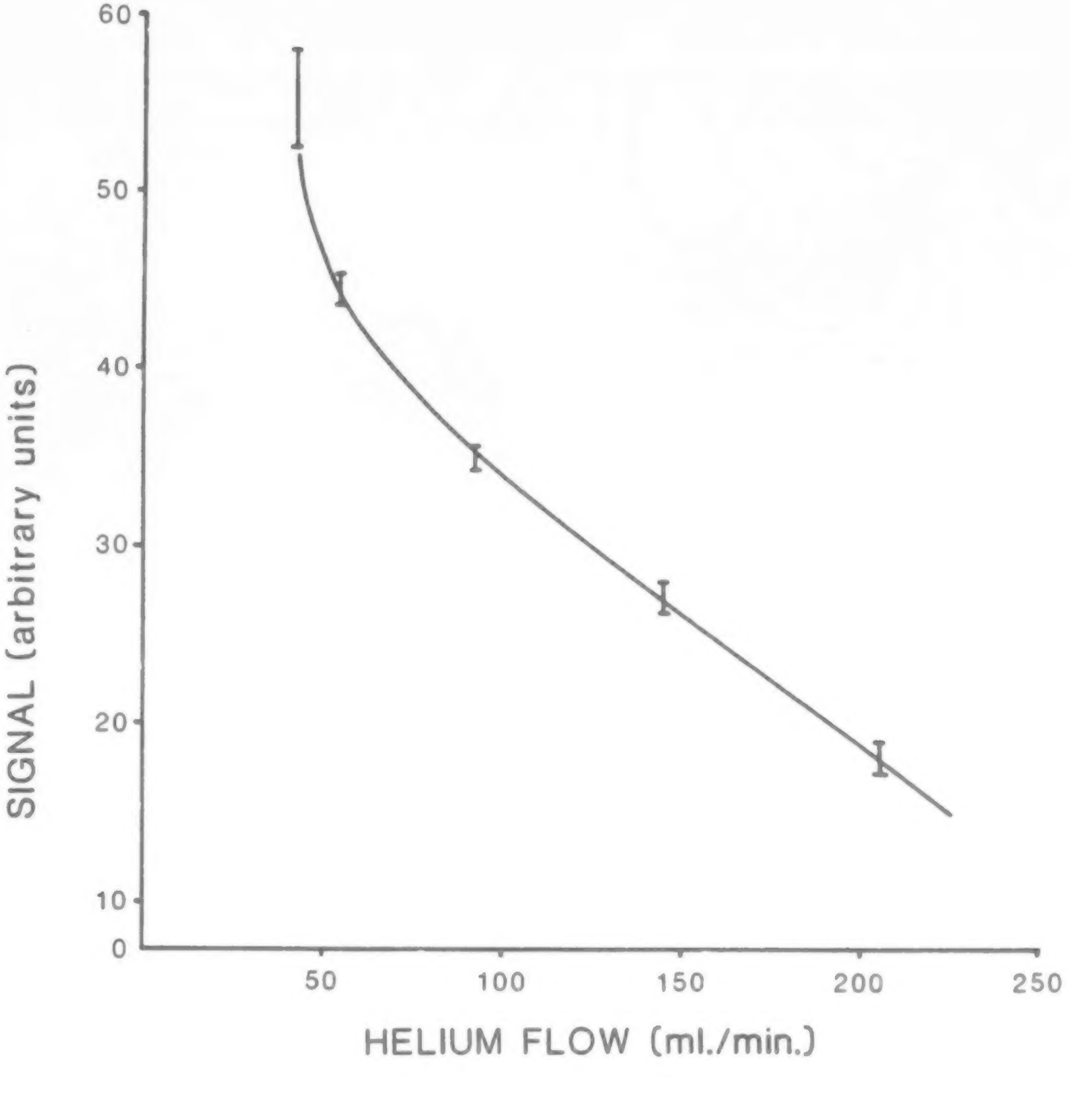

FIG. 7: Carbon Signal Versus Helium Flow
(incident power = 75 Watts)

Technology Transfer Conference
December 9, 1986
The Sheraton Centre, Toronto, Ontario

Presentation:

"Development of Methods Suitable for Use in the Ames Salmonella Mutagenicity Assay for the Collection of Organics Present in Groundwater and Landfill Site Matrix Materials"

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INTRODUCTION

There is a need for the development and validation of test protocols to assess the degree of leachability and mobility of potentially hazardous materials contained in landfill disposal sites. A detailed chemical analysis and identification of all chemical species in leachates and groundwater is desirable, but such survey type analyses are time consuming and costly. In addition, because of synergistic, antagonistic or other chemical and/or microbiological transformations which may take place in the environment, chemical analysis alone may not provide adequate assessment of the potential health risks involved.

Short-term biological tests are attracting interest as a basis for possible regulatory purposes. The reason is that these tests provide some predictive value regarding health effects. The overall goal of this program is to develop and validate concentration methods for organic chemicals from groundwater and solid matrix material for use with the Ames bioassay.

LITERATURE REVIEW

The initial phase of the study was a literature search undertaken to collect existing data regarding organic chemicals present in leachates and in contaminated groundwater or surface water associated with sanitary landfill or hazardous waste disposal operations. This was accomplished in three stages:

- Computerized searches of key words in numerous data bases including the following: QL, Toxline, NTIS, Enviroline, Environmental Bibliography, Chemical Abstracts, Pollution Abstracts, Water Resources Abstracts and D.O.E. Energy.

- Key papers were ordered from the references listed in the computer search. The papers were numbered, abstracted, filed and listed. Additional papers were ordered from the references listed in the key papers. This leachate Master List is being continually updated as the program continues.

- From the list, papers were selected for detailed critical evaluation. This applies especially to those papers dealing with organic chemicals found in landfill leachate/groundwater extracts. Special emphasis was also given to papers relating to methods used for the isolation/concentration of organic compounds present at low concentrations in aqueous solutions. In addition, papers relating to analytical methods used to characterize the organic content of solid matrix material from landfill sites received special attention.

From this literature review, lists of organic compounds were compiled. The lists were assembled so that they served several purposes.

- It provides an alphabetical reference of the various compounds identified at problem sites.

- It defines the pollutant group into which the compound falls, viz:

  1) conventional pollutants, e.g. COD, TOC, TOX, phenols, etc.
  2) priority pollutants (consent decree)
  3) Section 311 compounds
  4) Resource Conservation & Recovery Act [RCRA]
     (A - acute hazardous; H - hazardous; T - toxic)

- It classifies the compounds according to twelve (12) chemical classes similar to those used for priority pollutants.

  1) Alcohol
  2) Aliphatic
  3) Amine
  4) Aromatic - non-halogenated and halogenated aromatic compounds
  5) Ether
  6) Halocarbon-halogenated aliphatic compounds
  7) Miscellaneous - including selected priority pollutants, pH, BOD, TOC, COD, chloride, sulfate, phosphate, and other parameters generally used to characterize wastewaters.
  8) PCB
  9) Pesticide
  10) Phenol - including chloro- and nitro- phenols
  11) Phthalate
  12) Polynuclear Aromatic

- It specifies the ranges and concentrations encountered at actual hazardous waste disposal sites.

- It indicates frequency of occurrence at actual waste sites previously investigated.

In addition, the compounds listed were checked for positive mutagenicity/carcinogenicity activity. This was accomplished by comparison of the compounds listed with data present in appropriate mutagenicity references.

SELECTION OF CHEMICALS

Initially, it was necessary to select a limited number of chemical compounds for inclusion in an aqueous solution ("cocktail mix"). The purpose of this solution was to simulate, if possible, a landfill leachate in order to permit the validation of isolation/concentration techniques and measurement methods of the concentrates. The data acquired should provide information for predicting the behaviour of other related organic compounds when subjected to similar concentration techniques. The guidelines used for selecting the reference compounds were:

- to provide a wide selection of functional groups
- to represent, where possible, a range of pertinent physical properties such as volatility and polarity
- to choose compounds readily available in pure form at modest expense
- to avoid, where possible, multiple functional groups
- to choose, where possible, known water pollutants
- to select, when possible, halogenated derivatives of several parent compounds
- resistance to degradation
- to include known mutagenic compounds

The compounds selected for inclusion in the "cocktail mix" are listed in Table I. All the chemicals listed (with the exception of 2-Nitrofluorene) have appeared on lists relating to contaminants reported: viz. cancer risk assessment, chemical hazard information profiles (CHIP), and exposure assessments. The presumed mutagens on the list are indicated by means of an asterisk.

BIOLOGICAL PROPERTIES

Mutagenicity

One of the best known of the short-term bioassay systems is the bacterial test developed by Dr. Bruce Ames and co-workers in California. The assay uses mutant strains of the bacterium Salmonella typhimurium. Each strain contains a point mutation. This results in the mutant strain being unable to grow in the absence of histidine. In addition to the histidine mutation, each tester strain contains other modifications. One enables agents to permeate more easily into the bacteria. A second interferes with the bacteria's repair mechanism and permits the action of the mutagen to be expressed and detected by its assay.

Exposure of a tester strain to mutagenic substances results in some of the mutant cells reverting back to their wild state. In the process, the bacteria regain the ability to synthesize histidine and grow as colonies on histidine free media.

The frequency at which strains revert depends upon several factors, one of which is the potency of the agent tested. Mutagenic agents which are highly potent will induce a greater number of bacteria to revert than agents which produce less mutagenic damage. The addition of an activation complex is needed in some instances, as many substances which are non-mutagenic outside animal systems are structurally altered to a mutagenic form by metabolic processes within animal tissues. This function is accomplished in the Ames assay by the addition of a metabolic activation mixture (S-9).

Some investigators suggest bioassays are only useful when testing pure compounds because of problems associated with the interpretation of mutagenicity results. High concentrations of mildly toxic constituents or small quantities of highly toxic constituents in a complex mixture can suppress or prevent the detection of mutagenicity. The Ames bioassay has been used to assess the mutagenicity of complex mixtures, however, few studies have been conducted to evaluate how mutagenic compounds behave in mixtures. The nature of the compounds selected for the cocktail mix and those known to exist in landfill leachates required that we investigate whether the proposed program of developing a biological monitor was feasible. This feasibility study was accomplished by evaluating how the selected compounds behaved within a combination of mixtures.

Toxicity

Toxicity (i.e. concentration that kills bacteria) tests are used to establish the maximum concentration of a compound that can be tested using the Ames assay. Mutagenicity and toxicity are sometimes closely related and it is necessary to test up to a toxic dose when screening for mutagenicity.

EXPERIMENTAL

All analytical work that was to be undertaken (both biological and chemical) was to be performed at chemical concentrations that were considered realistic in terms of the concentrations that might be expected in contaminated groundwater. The concentration chosen for validation studies was 1 µg/L (ppb) of the organic compounds in aqueous solution. It was expected that 50 L water samples would be used in the extraction/concentration procedures to be used. Before proceeding with any extraction/concentration techniques, it was necessary to assess the biological properties of the selected chemicals at the appropriate concentrations being considered to ensure that biological testing could be accomplished. If one assumed a 100% recovery, a concentrate containing 50 µg of each of the chemicals could be expected. Therefore, in order to assess the biological properties of the selected chemicals, concentrates in dimethyl sulfoxide (DMSO) of 50 µg/mL of each chemical was used.

Biological Properties of the Compounds Selected for the Cocktail Mix

a) Toxicity

Each of the twenty compounds was tested separately to determine the concentration that was toxic to Salmonella tester strain TA-100 in the absence of metabolic activation. All compounds were dissolved in dimethyl sulfoxide (DMSO) and the maximum amount of DMSO applied was 0.1 mL per plate, which is below the solvent toxicity. Toxicity tests were carried out using 0.1 mL of 2×10^8 suspension of tester strain TA-100. The standard plate incorporation assay was performed. Toxicity was assessed microscopically by examination of the background lawn and by comparison of the number of spontaneous revertant colonies. Most of the solid compounds were tested at half log doses up to 1000 μg/plate unless prevented by solubility. The liquid compounds were assayed up to 0.5 mL (500 μL) per plate.

When all twenty compounds were mixed together at a concentration of 5 μg/plate and less, there was evidence of slight toxicity. The slight toxicity did appear to have an effect on the mutagenicity of the cocktail mix. The toxicity did not prevent detecting the mixture as positive and mutagenic.

b) Mutagenicity

The four selected mutagens were tested using the Ames Salmonella mutagenicity plate incorporation assay procedure to determine dose-response data. The mutagens were tested for their known positive conditions (strains, concentration and activation requirements) up to the level of toxicity. Two Salmonella tester strains TA-98 and TA-100 were used in this investigation. The results are recorded in Table III.

Three of the four selected mutagens (2NF, BNA and B[a]P) showed positive dose-responses between 0.1 and 10 μg/plate. The fourth compound DBE was a weak, direct-acting mutagen with a linear dose-response between approximately 1000 - 10000 μg (1 - 10 mg)/plate.

After confirming that the presumed mutagens were positive in the Ames test, an evaluation of their mutagenic activity using different combinations was conducted. The experiments conducted involved the following:

a) The selected mutagens were mixed in pairs over their positive concentration range and the results compared to the value expected from summing the individual responses.

b) The four selected mutagens were mixed over their positive concentration range and the results evaluated for additivity.

c) The "cocktail mix" was evaluated by testing the 4 mutagens, 16 non-mutagens and the full mixture at the same dose levels using TA-98 and TA-100 in both the presence and absence of metabolic activation.

The questions to be answered were:

1) Is mutagenic activity additive?
2) Is toxicity additive?
3) How do different mutagens (direct and indirect acting) behave in combination?

The tests for individual responses and combination responses were conducted at the same time. Each compound was tested over its positive dose range. The testing was conducted in triplicate at each dose and the average net revertants per concentration was calculated. This value is obtained when the average control value determined for the tester strain is subtracted from the average of the three replicates at each concentration tested.

Figures 1 - 8 show the mutagen combinations used and the results obtained in bar chart form. These experimental data will be discussed during the paper presentation.

CHEMICAL TESTING

Stock solutions of the individual chemicals were prepared by weighing known amounts of each and dissolving in a suitable solvent. Preliminary chemical data were obtained by direct injection of suitable aliquots (1-3 µL) of the individual compounds initially, and then of a combined mixture of the compounds into a gas chromatograph/mass spectrometric (GC/MS) system. The system used was:

> HP Model 5790A series capillary GC with an HP 5970A Mass Selective Detector. The data system was an HP ChemStation with an HP 9816S computer and HP 9133XV disc drive printer.

Instrument Parameters

(i) GC Conditions

Column : 30 m x 0.25 mm fused silica column (SP B5)
Injection : 250°C
GC/MS Interface : 250°C
Column Program : 50°C for 1 min; 10°C/min to 275°C
Carrier : He at 1.5 mL/min

(ii) MS Conditions

Source : Electron Impact with 70 eV
Electron Multiplier : 2000-2400 volts
Scan : 380 amu/sec; 4 samples per 0.1 amu
Mass Range Scanned : 35-400 amu

Data was obtained for all the compounds using both total scan and selected ion monitoring procedures. Either or both methods will be used for identification and quantitation during the validation of extraction-/concentration techniques for recovery of the "cocktail mix" chemicals from groundwater and solid matrix materials. In Table IV the compounds are listed together with their respective retention times and the major ions (m/e) present in their mass spectra.

TABLE I

ORGANIC COMPOUNDS SELECTED for "COCKTAIL MIX" to be USED in VALIDATION STUDIES for EXTRACTION/CONCENTRATION PROCEDURES for the ISOLATION OF ORGANIC COMPOUNDS from GROUNDWATER and SOLID MATRIX MATERIAL

● Alcohols (none)	
● Aldehydes (none)	
● Aliphatics	* 1,2-dibromoethane 1,2-dichloropropane
● Amines	* β-naphthylamine 3,4-dichloroaniline
● Aromatics	o-xylene 1,2-dichlorobenzene Hexachlorobenzene 4,4-dichlorobiphenyl
● Esters (none)	
● Ethers/Ketones	Methyl isobutyl ketone
● Carboxylic Acids	Isobutyric acid
● Phenols	o-cresol 2,4,6-trichlorophenol 4-nitrophenol
● Nitrogen Compound	Quinoline * 2-nitrofluorene
● Polycyclic Aromatic	Methyl naphthalene (α or β) Fluoranthene * Benzo[a]pyrene 9,10-dimethylanthracene
● Sulphur Compound	Benzothiozole
● Pesticides (none)	
● Phthalates (none)	

* known mutagen

TABLE II

Compound	Toxicity occurs between µg per plate			
Benzo[a]Pyrene		100	500	µg
2-Nitrofluorene		10	50	µg
Methyl-isobutyl-ketone		4000	8000	µg
Fluoranthene		5	10	µg
9,10-Dimethylanthracene	Not toxic		500	µg
4,4-Dichlorobiphenyl		100	500	µg
4-Nitrophenol		500	1000	µg
2,4,6-Trichlorophenol		100	500	µg
Hexachlorobenzene	Slight toxicity		50	µg
β-Naphthylamine	Slight toxicity		1000	µg
1,2-Dichloropropane		5780	11560	µg
1,2-Dibromoethane		10900	21800	µg
2-Methylnaphthalene		50	100	µg
3,4-Dichloroanaline		100	500	µg
Benzothiazole		1238	6190	µg
Quinoline		1093	5465	µg
Isobutyric acid		950	4750	µg
o-xylene		449	897	µg
o-cresol		1048	5240	µg
1,2-Dichlorobenzene		130	515	µg

The compounds (9,10-Dimethylanthracene 500 µg and Hexachlorobenzene 50 µg) were not toxic at their solubility limit. Two compounds (2-Nitrofluorene and 1,2-Dibromoethane) were mutagenic for tester strain TA-100 as tested in the toxicity assay.

TABLE III

Mutagenic Responses to Salmonella Tester Strains

Compound	TA-98 W/O S-9	TA-98 WS-9	TA-100 W/O S-9	TA-100 WS-9
DBE	Neg	Neg	Pos	Pos
2NF	Pos	Pos	Pos	Pos
BNA	Neg	Neg	Neg	Pos
B[a]P	Neg	Neg	Neg	Pos

TABLE IV

Gas Chromatographic and Mass Spectral Data for Chemicals in "Cocktail Mix"

Compound	Retention Time (min)	Base Peak in Mass Spectrum
1,2-dibromoethane	2.35	27
o-xylene	3.53	91
1,2-dichlorobenzene	5.84	146
o-cresol	6.27	108
Benzothiazole	8.99	135
Quinoline	9.20	129
2-methylnaphthalene	10.20	142
2,4,6-trichlorophenol	11.07	196
3,4-dichloroaniline	12.10	161
4-nitrophenol	13.57	139
β-naphthylamine	13.73	143
Hexachlorobenzene	15.81	284
4,4'-dichlorobiphenyl	16.72	222
Fluoranthene	19.74	202
2-nitrofluorene	20.26	165
9,10-dimethylanthracene	20.51	206
Benzo[a]pyrene	33.26	252

FIGURE 1

Mixture of 2NF + DBE
TA-100 without Metabolic Activation

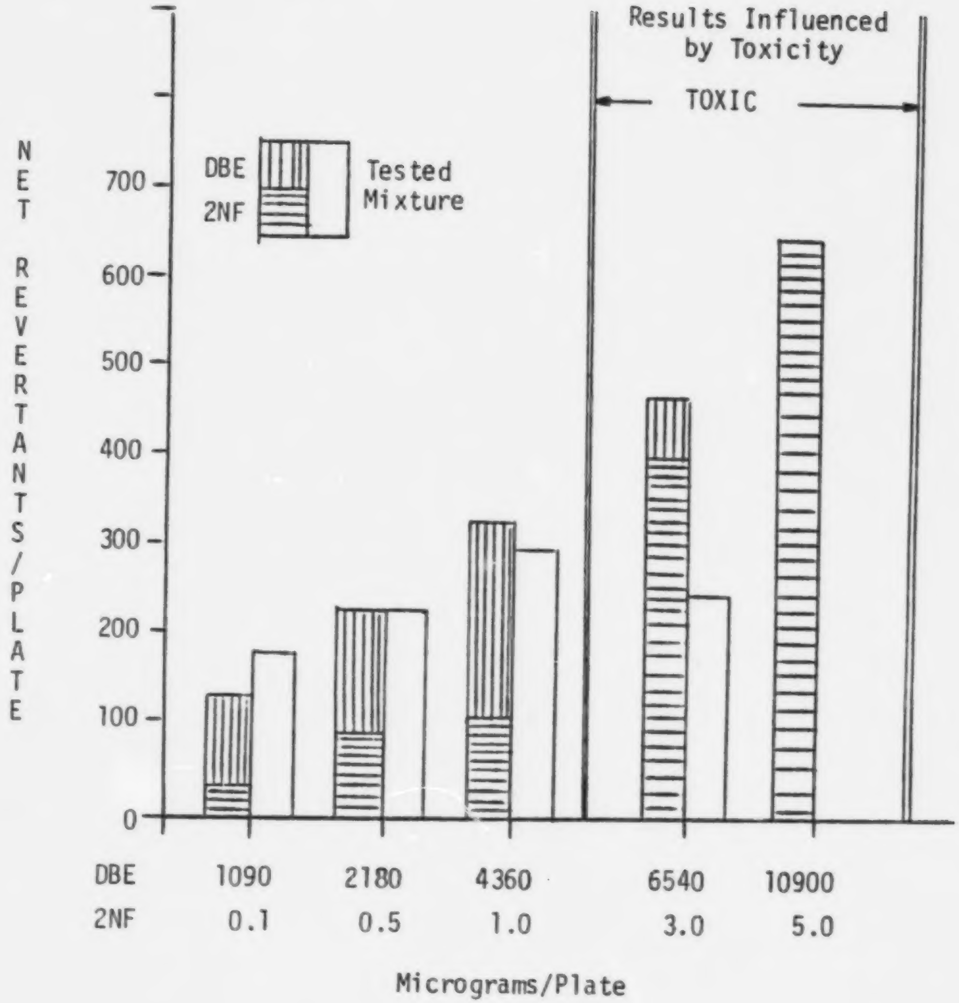


FIGURE 2

Mixture of BNA + DBE
TA-100 with Metabolic Activation

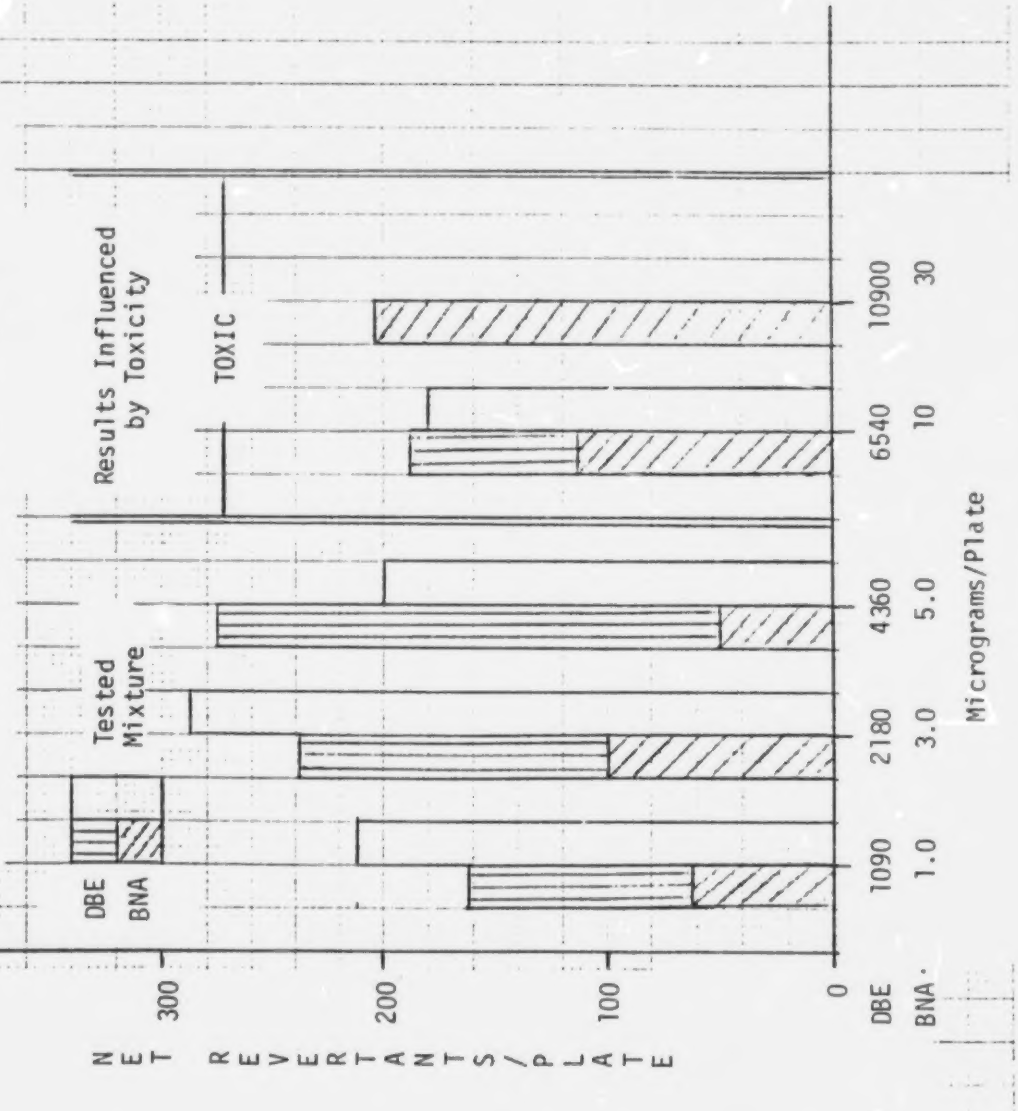
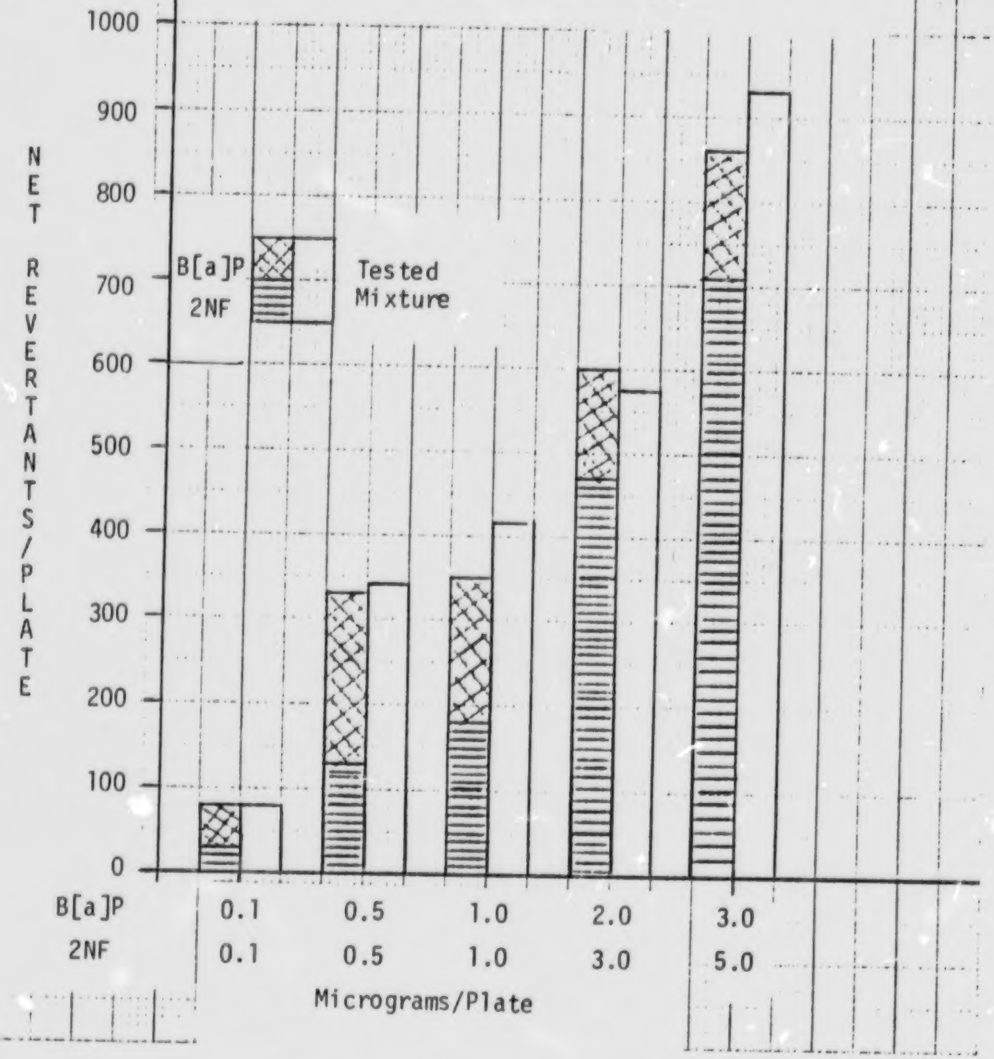


FIGURE 3

Mixture of 2NF + B[a]P
TA-98 with Metabolic Activation



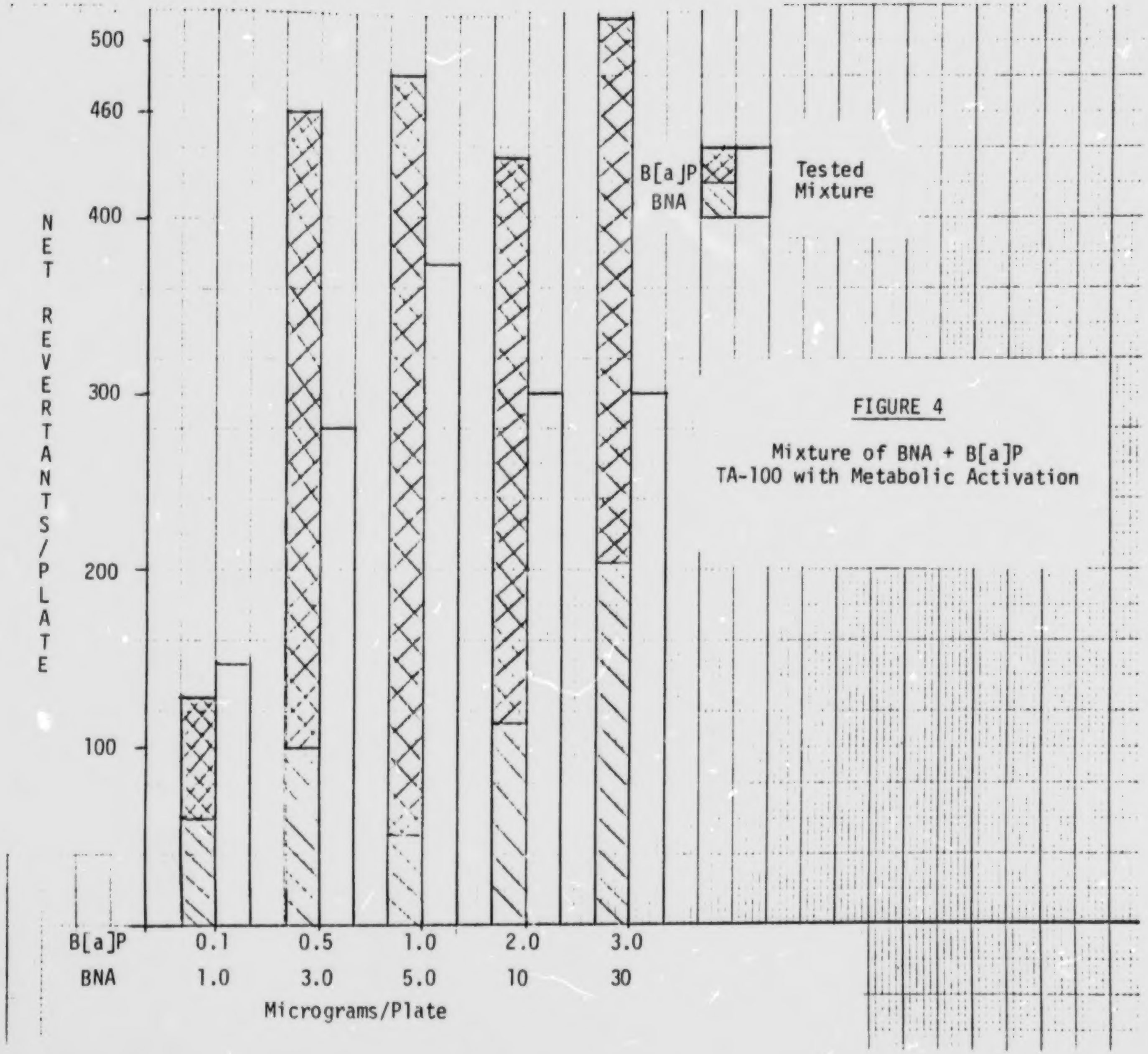


FIGURE 4

Mixture of BNA + B[a]P
TA-100 with Metabolic Activation

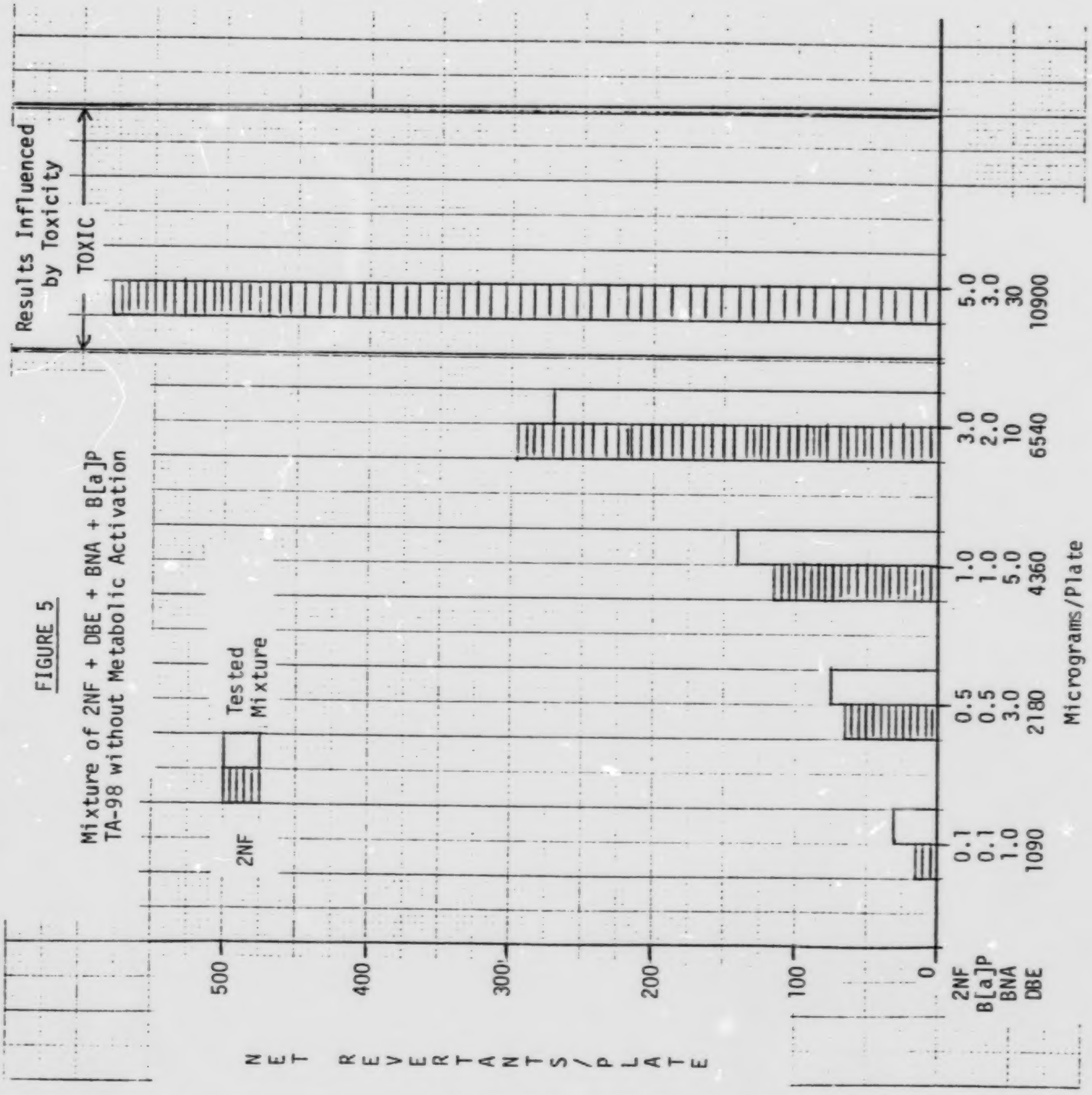


FIGURE 5

Mixture of 2NF + DBE + BNA + B[a]P
TA-98 without Metabolic Activation

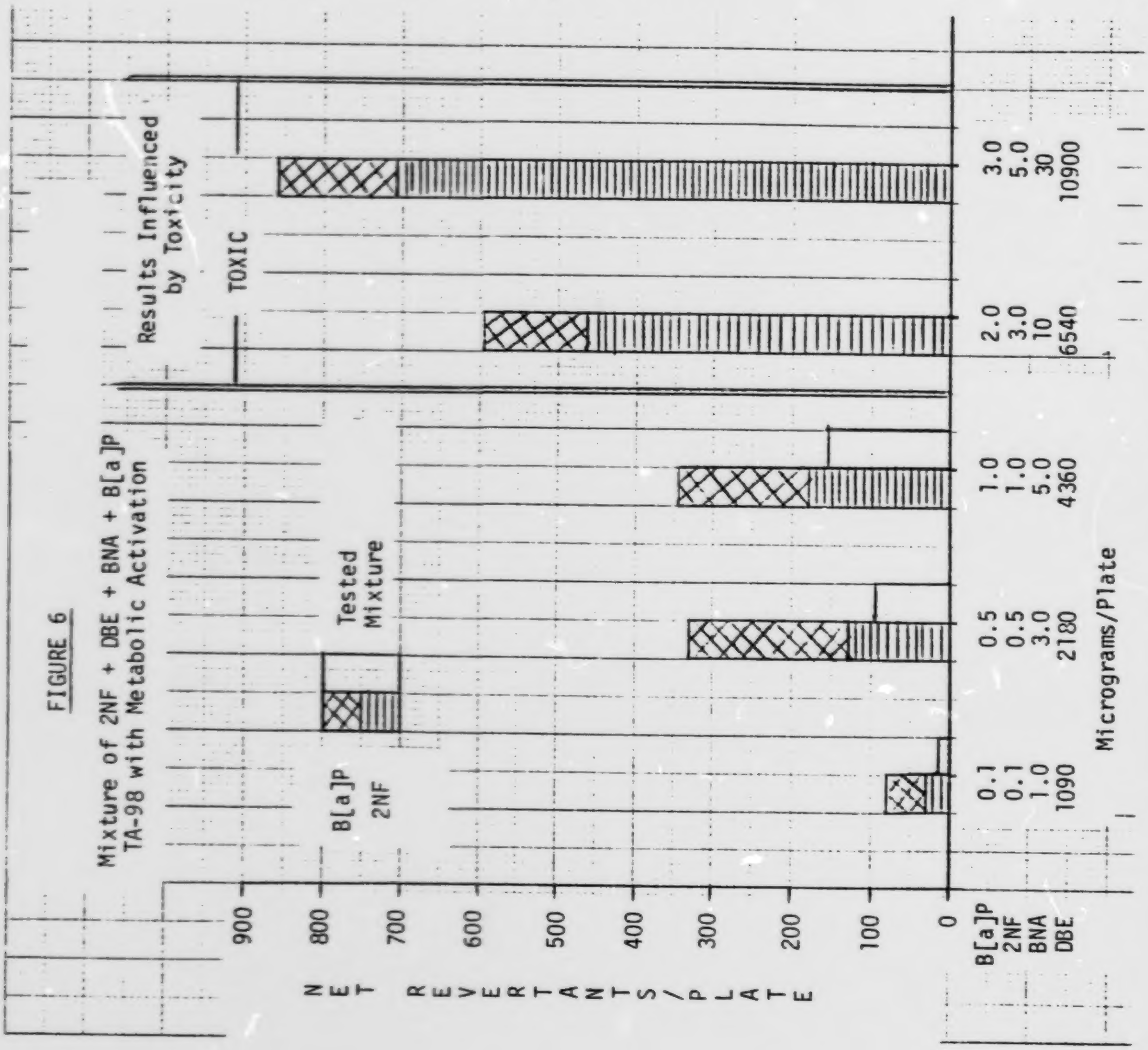


FIGURE 6

Mixture of 2NF + DBE + BNA + B[a]P
TA-98 with Metabolic Activation

FIGURE 7

Mixture of 2NF + DBE + BNA + B[a]P
TA-100 without Metabolic Activation

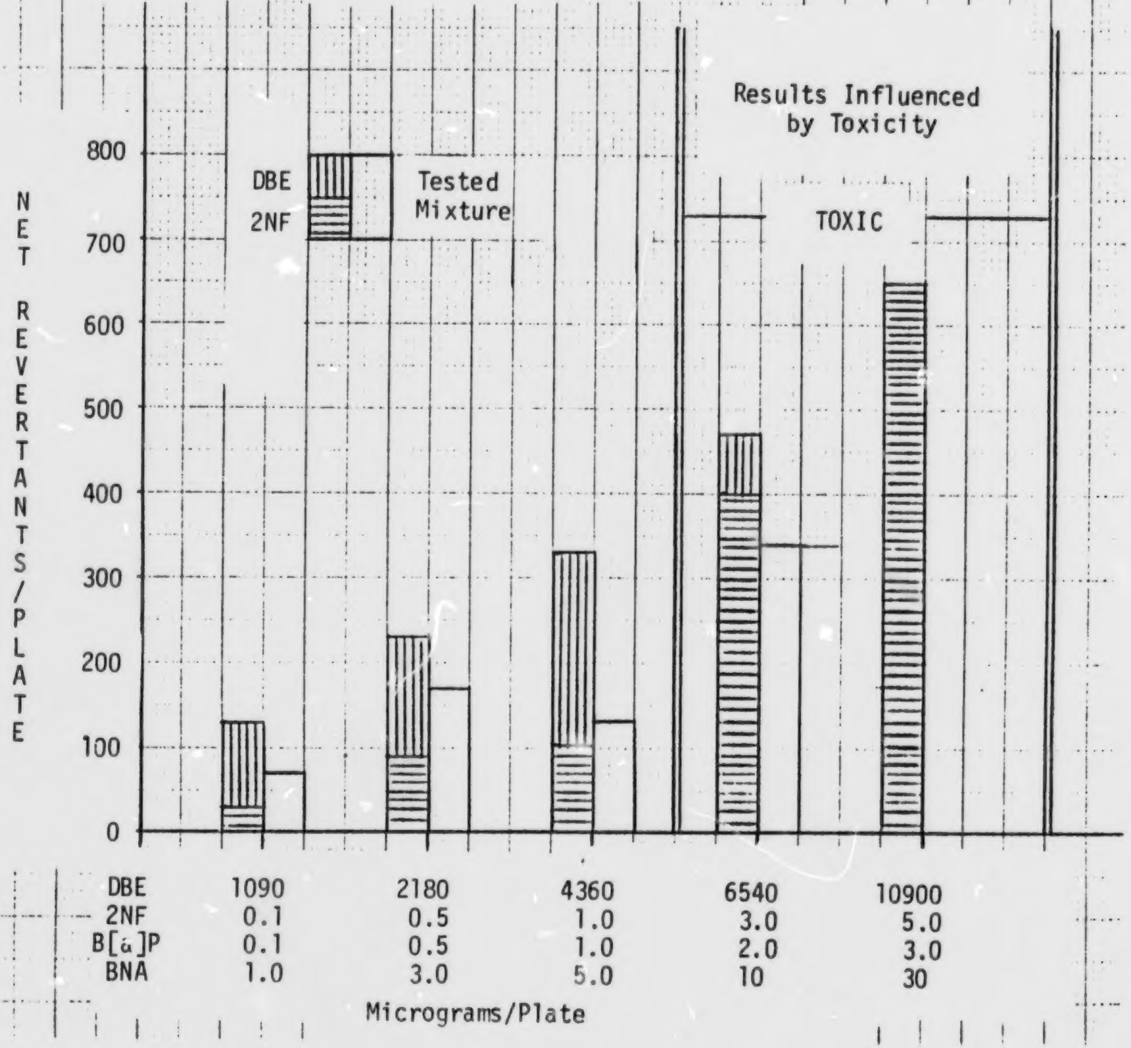
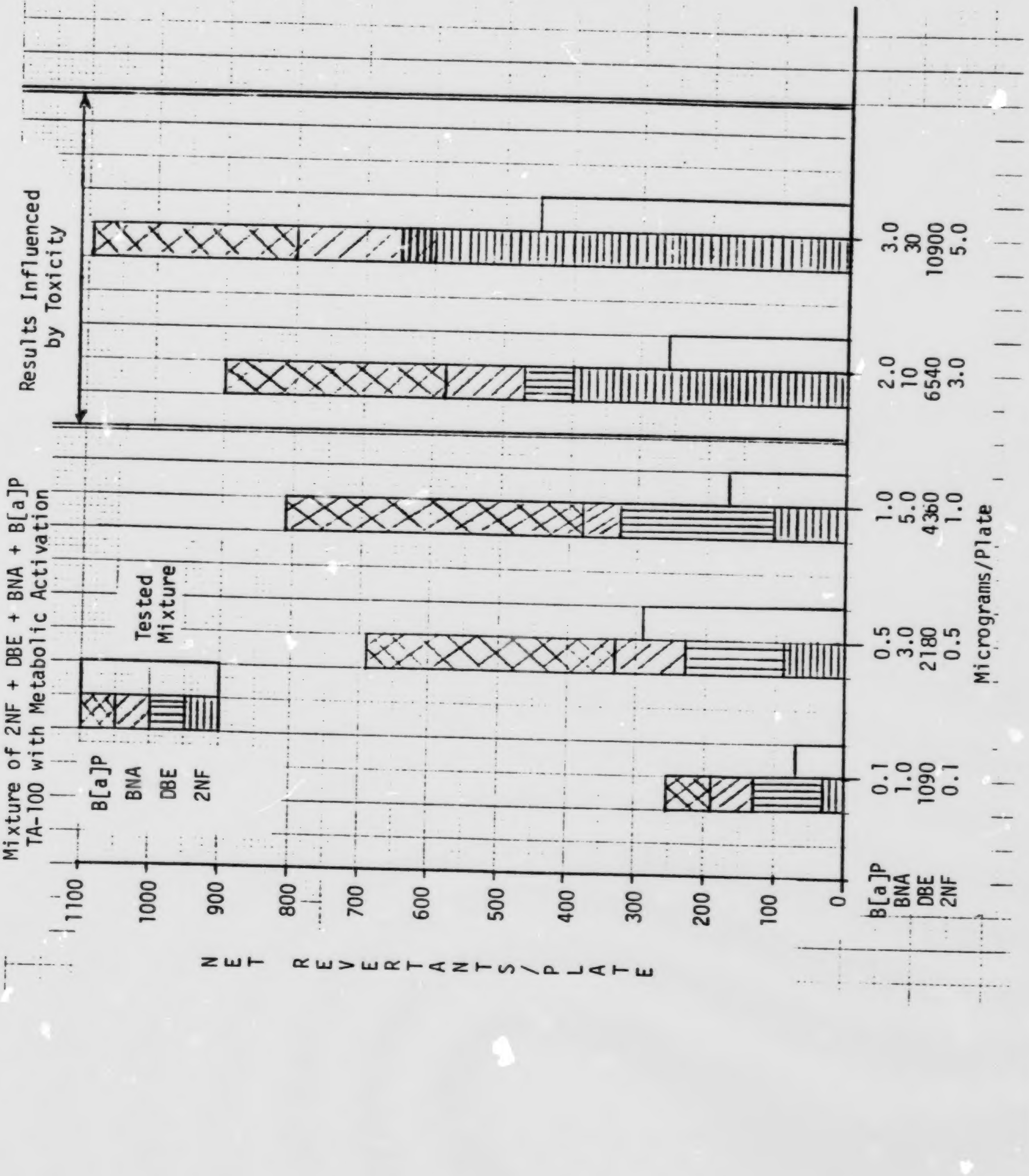


FIGURE 8

Mixture of 2NF + DBE + BNA + B[a]P
TA-100 with Metabolic Activation



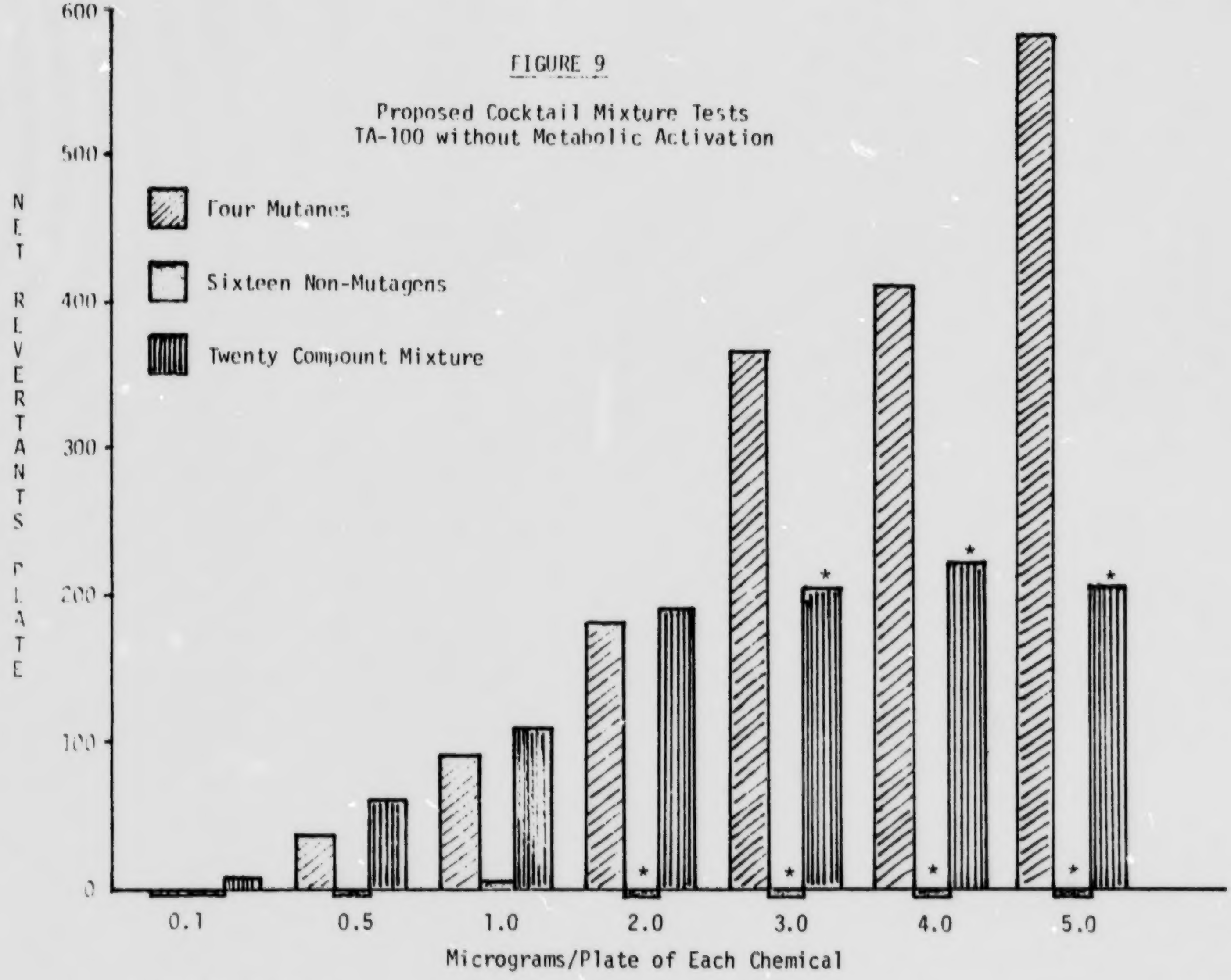


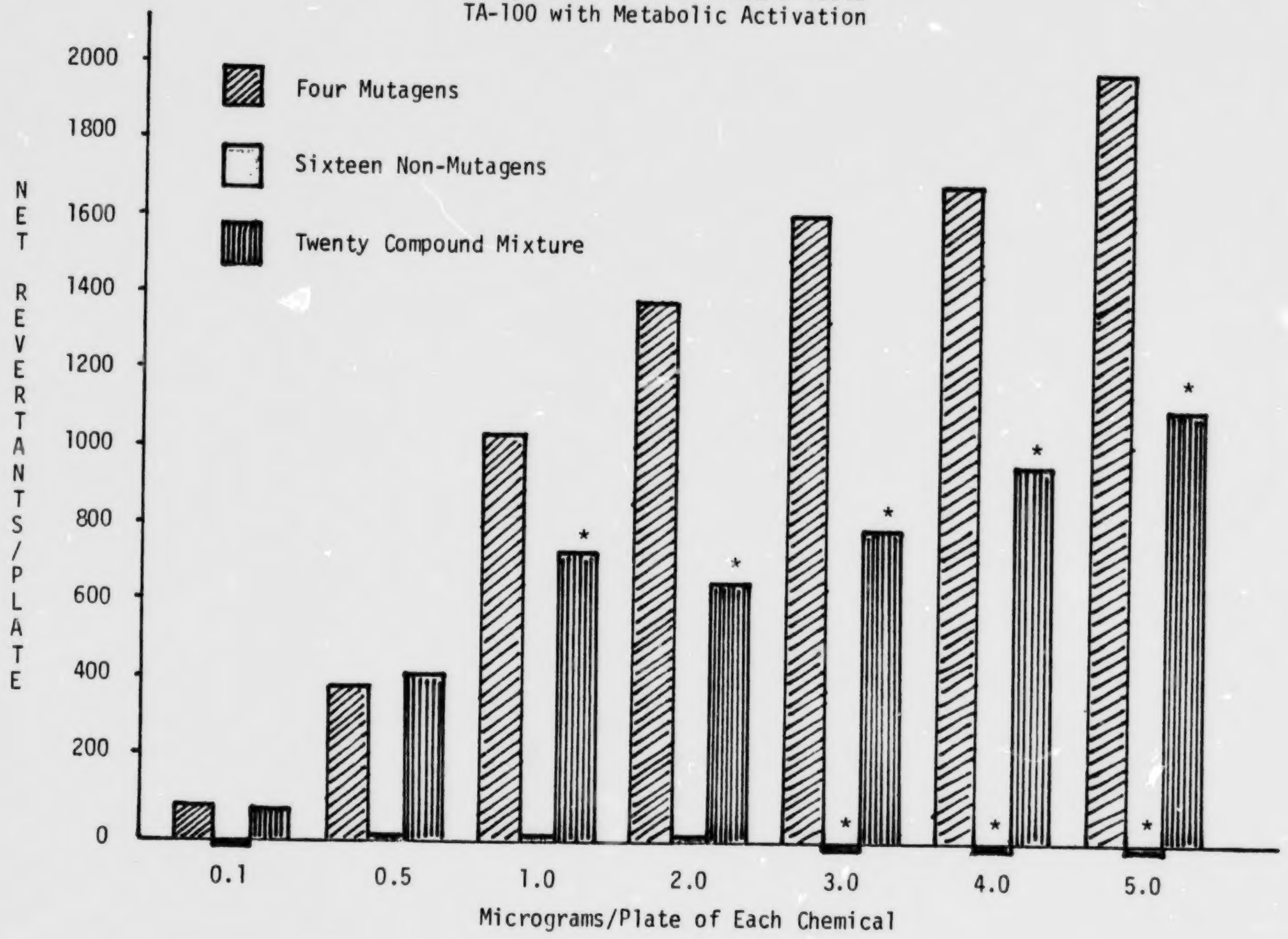
FIGURE 9

Proposed Cocktail Mixture Tests
TA-100 without Metabolic Activation

* slight toxicity

FIGURE 10

Proposed Cocktail Mixture Tests
TA-100 with Metabolic Activation



* slight toxicity

SYNTHESIS OF OXYGEN AND SULPHUR POLYNUCLEAR AROMATIC HYDROCARBONS OF INTEREST IN ENVIRONMENTAL POLLUTION

(Prepared for 1986 Technology Transfer Conference)

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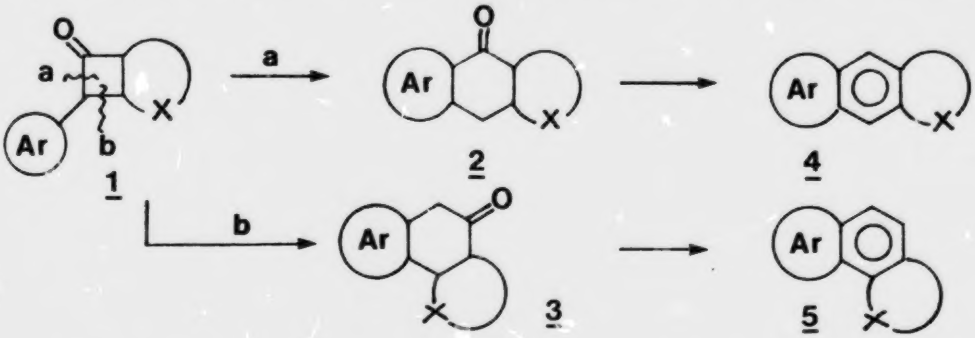
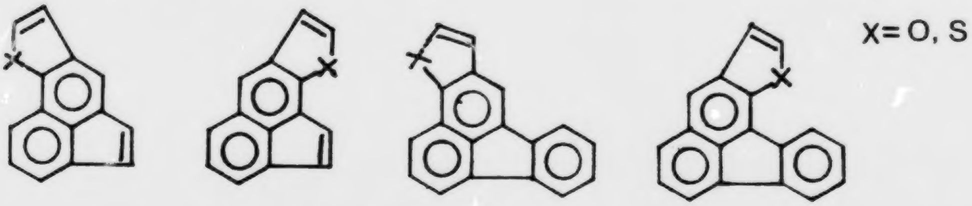
The occurrence of polynuclear aromatic hydrocarbons (PAH's) in the environment and their toxicological properties has prompted wide studies in both the environmental and toxicology fields[1]. Recently a number of cyclopentene annelated PAH's have been found to exhibit moderate to high levels of mutagenic activity[2]. Of particular interest have been the derivatives of cyclopenta(c,d)pyrene, a non-bay region hydrocarbon shown to possess significant levels of activity in the Ames test. The metabolic activation of these derivatives takes place by way of a peripherally fused cyclopentene epoxide and subsequent binding of the epoxide to nucleophilic sites in cellular macromolecules[3].

Moderate to strong mutagenic properties have also been associated with the seco derivatives aceanthrylene and acephenanthrylene[4]. In contrast to the carbocyclic systems relatively little is known about the biological properties of sulphur and oxygen heterocyclic analogues of mutagenic and carcinogenic PAH's primarily because of the lack of standards. In this study we report the synthesis of annelated benzofurans and benzothiophenes using two approaches which we have developed in our laboratory. The first approach involves the use of α-aryl substituted bicyclic cyclobutanones fused to a heterocyclic ring and the transformation of these intermediates by regiospecific ring-opening reactions to linear or angular fused PAH's[5]. The second approach involves the **S** or **O** cyclization of α-aryl or diarylmethylcations directly bonded to a thiocarbonyl or carbonyl group.

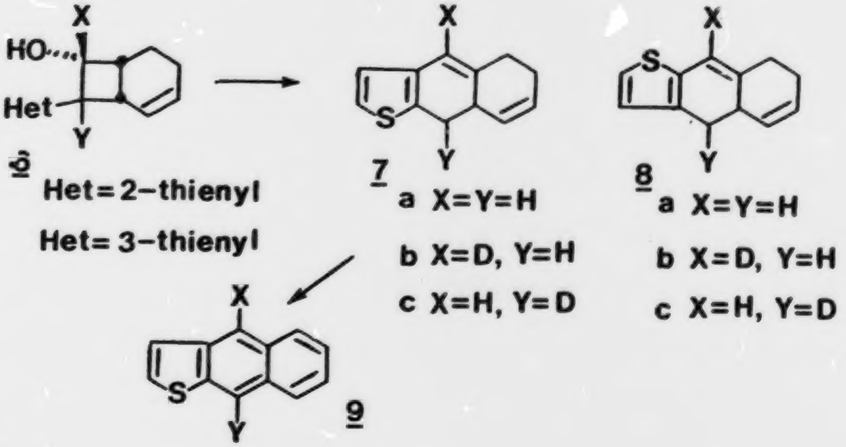
Regioselective ring-opening of bicyclic ketones **1** proceeds by α-cleavage in the presence of base (path a). The intermediate ester/acid can then be



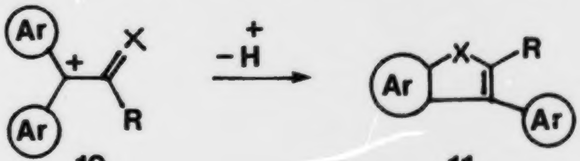
cyclized by standard methods to give ketone 2 which when reduced with LAH and dehydrated/dehydrogenated is transformed to the linear fused PAH 4. Alternatively, by treatment of 1 with acid under a variety of conditions the isomeric ketone 3 is formed (path b) and can be converted to the angular fused heteroaromatic system 5. Using this approach the following heterocyclic PAH's have been synthesized starting from the appropriately substituted bicyclic ketones 1:



In an effort to prepare bis heterocyclic PAH's we considered the possibility of using bicyclic ketones 1 in which the α-aryl substituent was part of another heterocycle. The initial studies were done on α-2 and α-3-thienyl derivatives of 1 in which the **X**-fused ring was a cyclohexene. The analogous reactions "a" and "b" did not proceed as efficiently as in the case of the carbocyclic α-aryl substituted ketones 1. In view of our previous studies[6] using cyclobutanols, analogous acid transformations and subsequent structural modifications led to the preparation of angular fused PAH's 5. We investigated the acid rearrangements of derivatives 6. These were efficiently transformed to the unexpected linear tetrahydro derivatives 7 and 8 which were dehydrogenated to the linear PAH 9. The mechanism for the formation of the unexpected linear derivatives 8 and 9 was elucidated by studies with specifically substituted deuterated derivatives of 6[7].



The second approach was based on work we carried out using diarylmethyl cations substituted with carbonyl groups[8]. These intermediates undergo fluorene cyclization in the case of the diaryl derivatives or oxygen cyclization depending on the nature of the carbonyl group (ketone or carboxylic acid derivative)[9]. Oxygen cyclization gives rise to annelated



benzofurans 11 (X=O). We have recently observed that diarylmethyl cations in which the cation is substituted with a thioformamide group rearrange exclusively to annelated benzothiophenes 11 (X=S). The mechanism for these transformations has been partially resolved by studies with unsymmetrically substituted diarylmethyl cations 10. Such cations 10 are routinely generated from the corresponding alcohols.

In conclusion, two independent methods have been developed in our labs for the preparation of annelated benzofurans and benzothiophenes. By appropriate substitution of the precursors a wide variety of these heterocyclic PAH's can be obtained.

We would like to thank the Ministry of the Environment, Province of Ontario, ARB for their generous support of this project.

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DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL TISSUES USING ACID DIGESTION AND SOLVENT EXTRACTION METHOD

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1.0 INTRODUCTION

The increasing concern over the presence of persistent toxic chemicals in the food chain has led to an increase in the number of analyses that must be performed annually. However, due to the current fiscal climate, available resources have not kept pace with this increase in the workload.

As is the case with most types of analytical work, the sample preparation step is usually time consuming and prone to error. To alleviate this bottle-neck, a robotic sample preparation system is being developed.

The system being used to implement this procedure is the Zymate II Laboratory Automation System, manufactured by Zymark Corporation of Hopkington, Mass.

The system design objectives are as follows:

i. Improved precision and accuracy of results.
ii. Cost savings in materials such as solvents.
iii. Reduced operator exposure to hazardous chemicals.
iv. Improved data reduction and reporting.
v. User friendliness.

The development of this system involved precise specification of a robotic method based on a manual procedure, the acquisition and modification of the hardware required by the method, the design and testing of software, and validation of the completed system.

This paper presents the progress of this project at the time of writing. Further evaluation will be undertake to assure that all design requirements are met.

2.0 SYSTEM HARDWARE

After evaluation of the manual method, the hardware components decreased necessary to convert to an automated method were as follows:

(i) Robot arm and Controller
ii) IBM-compatable PC
iii) Master Laboratory Station and Remote Pipetting Kit
iv) Electronic Balance
v) Sample Conditioning Station (Linear Shaker)
vi) Capping Station
vii) Centrifugation Station
viii) Drying/Neutralization (Prep_Sep) Station
ix) Waste/Rinse Station
x) Assorted Racks
xi) Printer

2a DESCRIPTION OF WORKSTATION COMPONENTS

a) Robot Module

The "robot" itself consists of an "arm" secured to a benchstop by a pedestal. This allows three degrees of freedom of motion. The arm is capable of holding a variety of "hands", which rotate about a wrist connection, giving one extra degree of freedom.

The range of motion in each direction is:

(a) Vertical : 0-34 cm
(b) Reach : 0-32 cm
(c) Rotary : 0-376^0

The arm's locomotive power is provided by a wire pulley system, driven by DC servomotors. Directional control is provided by programmed commands. Initial calibration of the arm at the factory provides a frame of reference, so the arm "knows" it's current position. To go to a new position, the controller compares the current position to the desired position. This generates an error signal, which drives the servo's in such a way as to minimize the error signal.

There are four different types of hands available to this system:

(a) General Purpose Hand
(b) Syringe Hand
(c) Dual Function
(d) Blank Hand

In this application, the General Purpose Hand and the Blank Hand are used.

The General Purpose Hand consists of a teflon block housing a servomotor and has two "fingers" (grippers) attached. This hand is used for manipulation of glassware. The joint of the hand and arm forms a "wrist" capable of rotation form -5 to 365^0. In addition, the force with which the fingers grip an object can be adjusted from 0 to 200 units.

The arm and hand assemblies can also receive feedback from the external world in each of three axis:

ie: Vertical Force
Reach Force
Rotary Force

as well as Grip Force in the hand. This allows the arm to "sense" possible error conditions while performing operations on the bench.

The arm also allows different speed settings for each axis and can sense a collision, in which case it stops, and can only be restarted by operator intervention.

b) Master Laboratory Station and Remote Pipetting Kit

(i) The Master Laboratory Station consists of a housing containing three 10ml syringes, valving to control fluid flow, stepper motors to drive the plungers, and a dispenser nozzle mounted on a post.

The syringes can be programmed either independantly or jointly, to dispense/fill from a reservoir. Plunger speed can also vary to compensate for fluids of different viscosities.

The Dispenser nozzle contains separate outlets to avoid cross-contamination of liquids.

The syringes are programmed by "setting" the volume, speed and flow conditions necessary in a given operation.

Accuracy and precision for this station are quoted at 0.5% and 0.2% respectively, where volumes are greater than 20% of total syringe volume.

(ii) Remote Pipetting Kit

The remote Pipetting Kit allows pipetting/dispensing to vessels at fixed positions on the benchstop. It consists of a Blank Hand with a pipet-tip holder and pneumatic shucker, the parking station for this hand, and tubing for attachment to external compressed air, the MLS, solenoid operated valve, and a pipet-tip rack.

After attachment of this hand, programming is the same as for programming of any other robot moves. The pipet-shucking operation is driven from the Power and Event Controller, where actuation is by switch closure.

c) Power and Event Controller

The Power and Event Controller permits programmed operation of external devices. It provides the options listed in the following manufactures documentation.

In this application, it is used to disgard pipet tips and operate vacuum for the Rinse/Waste station. The large number of control functions will permit future expansion to the system, should it be required.

The Power & Event Controller

The Power & Event Control module provides programmable control of laboratory devices external to the Zymate System. This module consists of:

- 8 isolated relay contacts for device control
- 8 logic inputs that sense high/low voltages or switch closures
- 2 on/off 115 VAC power outlets
- 1 variable AC power outlet
- 1 analog/digital converter that accepts a 0 to 2V analog signal from devices monitoring outside factors
- 3 power supplies (+5V, +12V, -12V) which provide additional sources of power for external devices

SPECIFICATIONS

SWITCHED OUTPUTS:

Relays	Reed Switch, Glass Enclosed

Contact Ratings
1/2 Amp. Max - DC or AC RMS
24 Volts Max - DC or AC RMS

SENSED INPUTS: (TTL Compatible)

Resistor	4.7K Pullup
Voltage, open circuit	5.0

Current, external switch closed, 1.0 ma

A/D INPUT:

Input Range	Ground to +2V
Converter	
Increments	1 mV
Precision	+/- 0.1%
High Input Impedance	
Sampling Time	1 sec

SWITCHED A.C. OUTPUTS:

At any one time, no more than 5 amps or 600 VA TOTAL may be drawn from all 3 AC outlets

VARIABLE A.C. OUTPUT:

At any one time, no more than 5 amps or 600 VA TOTAL may be drawn from all 3 AC outlets

POWER SUPPLIES

5V	1/2 A
+12V (adjustable: 2 to 12 V)	1/2 A (decreases as voltage decreases)
-12V (adjustable: -2 to -12 V)	1/2 A (decreases as voltage decreases)

d) Printer Module

The system permits operation of a printer to provide hard copies of data and programs. It can be programmed to be either enabled or disabled and provides essentially a line by line screen dump.

e) Balance Module

The balance used in this application is a Mettler PE200. The module consists of the Balance Interface Card, a 5-pin to 32-pin cable and a sample tube holder. The balance is capable of sending weight results to the Controller via the balance interface card, which is compatible with Mettler's CL interface and capable of receiving commands from the controller. It is a menu-driven progammable unit, where baud rate, parity and data transfer Mode may be set and stored. In addition, dampening functions may be set to compensate for vibration and time-averaged readings are also possible.

Operation is from the controller, where weight and tare commands are defined. Results are stored in arrays for use in calculation of masses.

f) Capping Station

The Capping Station consists of the capper (an enclosed motor with a set of jaws on the top surface), and a cap parking station, where bottle caps are temporarily held.

The Capper's operation must be carefully coordinated with that of the arm. During a cap operation, a cap is retrieved from the parking station and lowered onto the tube while the capper rotates. Similarly, during an uncap operation, the tube is placed in the capper, the jaw grips the cap and the capper rotates in the opposite direction while the arm is incrementally raised.

The station can be programmed for

(i) Capping Torque

(ii) Number of Turns required to uncap/cap

Error routines are incorporated into the software to detect most common types of errors i.e. grip slipping.

g) Drying/Neutralization Station

This station consists of:

(i) a prep-sep dispenser
(ii) a prep-sep workstation

It is run from the PEC, where a switch closure will result in pressure being applied to a prep-sep containing a solvent aliquot. The prep-seps contain a layer of sodium bicarbonate (0.5g) and a layer of anhydrous sodium sulfate (0.5g). The pressure forces the solvent through the prep-sep, where the aliquot is dried and neutralized.

This workstation will save the expense of a powder pouring station and it's associated equipment as well as limited bench space and time during the running of the application.

h) Sample Conditioning Station

The Sample Conditioning Station consists of a linear shaker and two vertical, five position rack. The station is used for the agitation of samples during digestion and extraction, where the arm will load the tubes in a horizontal position.

The shaker is capable of speeds from 1 - 100 units and always stops at the same position, to faciliate access by the robot arm during insertion/removal from the rack.

i) Waste/Rinse Station

The Waste/Rinse Station will be used to aspirate the fish/acid residue and unused solvent to a waste holding tank. It is run from the PEC, where switch closure results in vacuum being applied.

The Rinse part of this station consists of a Hi-Volume Dispensing Kit, which contains a high-speed peristatic pump, tubing, valving, post and dispenser nozzles. When switched on, the tube will be washed out with water, supplied by the pump.

The Centrifuge Station

The Centrifuge Station adds automated centrifugation to the Zymate System. The Centrifuge Station offers a choice of two rotors: a 4 position rotor accepting tubes up to 50 ml in size; or, a 6 position rotor accepting tubes up to 15 ml in size. The Centrifuge Station operates at speeds between 300 and 3000 rpm with weights up to 100 grams per rotor position.

The Centrifuge Station will detect loads that are unbalanced, when the desired speed cannot be attained (within 50 rpm) or when its door is open. These conditions will cause a spin in progress to be aborted. Also, a spin will not be started with the door open unless the automatic door successfully closes.

There are a few sample load requirements in order to assure a successful centrifugation:

- The rotor must never be run with buckets empty or other uneven (though balanced) loads.
- All loads must balance within 1 gram.

This station provides programmable control of:

1. Rotor speed (up to 3000 rpm)
2. Spin time (up to 99.9 minutes)
3. Sensing of error conditions (out-of-balance, inability to reach speed, inability to find position, door opened during spin, door jammed)
4. Tube position

These programming controls may be set on a programming screen for direct operation of the Centrifuge Station. Or, command variables whose values are defined during the running of a program or in the Direct Control mode may be named.

2b OUTLINE OF SYSTEM CONTROLLER

a) Hardware

The Zymate II System employes several 16-bit chips. The main CPU is the Intel 8088, with an 8087 used as a math co-processor (the Fast Math upgrade from the Zymate I). Memory is 64K, with the operating system occupying 4K, leaving 60K for user applications. RAM in this system is non-volatile, battery-supported.

The Zymark System is very flexible due to the modular concept employed in it's design. In this design, each module (ie Capper, MLS) has it's own module card, where it's intelligence is contained on ROM chips. The module card is linked to it's module by a control cable, and to the controller by module support boards. Each module support board can hold up to five module cards, and there is room for five module support boards, hence, we may have up to 25 modules in a given application.

The System may be interfaced to an external computer by use of the Computer Interface Module. This module provides an RS232/423, ASCII, serial communications link between the controller and an external, more powerful laboratory computer. The interface parameters that may be set are:

(i) Baud Rate : Up to 1200 Baud
(ii) Character Length : 7 or 8 bits/character
(iii) Stop Bits : one or two

This will allow the Computer Interface to "talk" to almost any PC we choose to use, providing it has a communication board and uses the same RS 232 standard.

b) Software

The Zymate II System provides a menu-driven system for operator convenience.

Upon initialization of the system, the Controller polls the modules plugged into the module support boards, and configures the system accordingly. The initial menu is displayed, and gives one five choices:

1. Run Program
2. Edit Program
3. Bench and Module Set-up
4. System Management
5. Direct Control

1. Run Program: allows one to execute an existing EasyLab Program.

2. Edit Program: allows one to edit or create programs. This is a line-editor, sufficient for most purposes.

3. Bench and Module Setup: this selection displays the modules currently configured in the system. From this menu, we may enter a control "page" which gives direct control over that particular module.
Each module has a control page where defaults are set or changed. An example is the computer interface, where the baud rate, parity and stop bits may be set, depending on the characteristics of the external computer.

4. Systems Management: displays the status of the RAM batteries, amount of dictionary space left, and allows one to specify an autostart program.

5. Direct Control: allows the execution of programs, commands directly.

The Zymate II allows programs to be written in it's language called EasyLab. This is an interpreted language and has a flavor characteristic of BASIC. For example, the following constructs are allowed:

(i) Arrays: numeric, single dimension only.

(ii) DO Loops

(iii) GOTO's

(iv) IF conditions THEN statements : but no ELSE construct.

(v) Real Math: 6 Significant figures.

(vi) Standard Mathematical Functions : SIN,COS, ATAN, SQRT, LOG 10

EasyLab allows any user-defined variables to be globally available to any sub-routine called from within any program. The maximum number of levels of calls is limited to 7. Text processing is very limited, as there is only one type of PRINT statement.

To overcome the programming limitations of Easy Lab and the Controller, an external computer will be linked to the controller via the computer interface. With this configuration, a much more "intelligent" system can be designed, where the external computer can be executing a more complex program, and simply pass the appropriate commands to the controller. Likewise, the controller will pass information back to the computer, where decisions will be made.

The choice of a high-level language running on the external computer is essentially wide open, but QUICK-BASIC, a compiled version of BASIC, was recommened.

3.0 CHANGE TO MANUAL PROCEDURE

The currently used manual method is outlined in Appendix A.

In order to implement this method as a robotic procedure the following modifications were made:

i. All manual extractions are carried out in 60 ml centrifuge tubes. Since the capacity of the centrifuge module is only for 50 ml tubes, all volumes had to be adjusted accordingly.

ii. Robotic pipetting procedures are performed gravimetrically.

iii. In the manual procedure, extract neutralization and drying steps are performed in Evlenmeyer flasks. To implement this step in the same manner would require too much bench space and additional glassware to be manipulated by the arm. In addition, the dispensing of powders are sufficiently time-consuming as to reduce system throughput. Our solution was to proceed with disposable columns packed with sodium bicarbonate and anhydrous sodium sulfate, which requires only one additional workstation.

iv. The inclusion of a centrifuge module to break up emulsions and settle undigested fibrous material enables better separation of phases.

v. The manual procedure requires the final extract to be volumetrically diluted to 100.00 mls. A one gram equivalent (or 1/5 of total volume) is removed for cleanup. Again, table space does not permit the required number of flasks. Instead, the total volume of extract is computed and a calculated volume is pipetted volumetrically.

4.0 UNIT OPERATIONS OF SYSTEM

The following is a detailed description of the robotic steps performed in the method:

i. The initial step consists of taring a rack of capped, empty centrifuge tubes, which will be loaded with samples. This step is performed independantly of the main run sequence. All weights are stored in an array.

ii. After taring, the operator removes the rack of tubes and loads each with 5.0 ± 0.1 g of wet fish tissue.

The tolerance of the weight must be adhered to, in order to ensure the centrifuge remains balanced. The loaded rack is replaced on the table and the run is initiated.

iii. A sample tube is taken from the rack, and weighed to obtain actual sample weight.

iv. The tube is uncapped, acid is dispensed, capped and weighed.

v. The tube is then loaded into the linear shaker and digested for 1/2 hour.

vi. After digestion, the tube is unloaded from the shaker, uncapped and extraction solvent added.

vii. The tube is then capped, weighed (to obtain accurate weight of solvent added) and returned to the shaker.

viii. The sample is then extracted for 1 hour.

ix. After extraction, the tube is unloaded from the shaker. The arm then loads and balances the centrifuge. The sample is spun at 2500 rpn for 10 minutes to breakup any emulsion that may have formed and to settle out any undigestable fibre in the extract.

x. The sample tube is then unloaded from the centrifuge and the balance tube replaced. The sample tube is then uncapped, placed on the balance and weighed (as a check). A holding tube covered with a gravity slip-cap is picked up from the rack, it's cap removed and placed in the prep-sep work station. A prep-sep is then obtained from the dispenser and loaded into the prep-sep work station. The general purpose hand is then parked, the blank hand picked up and a 10 ml pipette tip is obtained form it's rack.

xi. To quantitatively pipette the extraction solvent, the arm positions the pipette tip over the tube on the balance and finds the surface of the liquid. Once this initial starting position is found, 95% of the solvent is drawn into the pipette and the arm then positions the pipette over the prep-sep, where the solvent is dispensed. The solvent is then slowly forced through the prep-sep, while the arm draws the remaining 5% slowly and accurately. The remaining solvent is then again dispensed and forced through the prep-sep.

xii. The pipette tip is then disgarded, and the blank hand is exchanged for the general purpose hand.

xiii The prep-sep is then also disgarded, the holding tube removed from the prep-sep work station covered with gravity slip-cap and returned to it's rack.

xiv. The arms returns to the balance and removes the sample tube which at this point, is still uncapped.

xv. A second aliquot of extraction solvent is added, for the second extraction; the tube is capped and weighed.

xvi. Steps viii - xi are repeated for the second extraction.

xvii. The pipette-tip is disgarded and the general purpose hand is picked up.

xviii. The prep-sep is disgarded, the holding tube is returned to it's rack, the sample tube is removed from the balance and it's contents are aspirated to waste. It is then returned to the sample tube rack.

xix. The general purpose hand is then parked and the pipetting hand is again picked up. Another pipette tip is attached.

xx. The arm then positions itself over the holding tube, and since the volume of solvent is known, positions the tip slightly below the surface of the extract. The volume of a one gram equivalent is calculated and drawn.

xxi. The arm then positions itself over the output tube, and the one gram equivalent is dispensed to the output tube. These tubes are not capped as the next step is the evaporation of the extract to dryness: (part of the subsequent manual cleanup).

xxii. The pipette tip is then disgarded and the general purpose hand picked up. The holding tube is then gripped, it's slip-cap retrieved and returned to it's rack. The system is then ready to proceed with the next sample.

This outline lists the robotic steps performed on a sample in a sequential manner. However, to use each work station to it's greatest potential (i.e. minimize idle time) the system runs as a serialized procedure. This requires that modules such as the shaker and centrifuge operate independantly of the arm, so in effect the system idle time is minimized. This was accomplished by fine-tuning the timing of each step so that synchronization between the arm and the modules was achieved.

In addition, at critical steps such as capping and getting a pippette tip, confirm operations are carried out to ensure the proceeding step was successful before the subsequent operation is carried out.

5.0 PROGRAMMING CONSIDERATIONS

As much as possible, error detection and correction routines have been built into the software. For example, due to variations in tube volume and sample size, the surface level of the extraction solvent will vary. Thus, the routine to find the initial starting point at which to begin a pipette operation is necessary. It was also discovered that the pipette tips are not perfectly straight and so may touch the wall of the tube. This results in an increasing weight reading during pipetting. The solution is to minutely shift the position of the arm in the horizontal plane until no more contact occurs.

The concurrency issue also arises, since under a serialized procedure samples will be at different stages of processing at the same time. This could lead to situations where different samples are competing for the same module. A good example is the balance, where one sample requires it for a pipette operation, another to obtain a sample weight and yet another to obtain a solvent weight.

The solution is to time balance the procedure so that each resource is available at the correct time. This involves the use of expiration timers for each sample at each module and avoids the use of priority interrupts. This also guarantees an identical processing history for each sample, one of the major requirements of any automated procedure.

Another requirement of this system is the processing of sample data and text. To accomplish this, an IBM compatable P.C. was linked to the controller to provide:

i. a menu-driven user interface to the system.
ii. expanded data storage and processing capabilities to the system.
iii. enhanced error-recovery.
iv. uploading of data to other systems.

This way the controller functions as a transparent low-level module, while the P.C. functions as a high-level controller, responsible for data reductions, file manipulation and repeat production.

6.0 ESTIMATED SAMPLE THROUGHPUT

The breakdown of robotic moves and times is given in the Table below:

	Operations	# Moves	Time
i.	Get tube from Sample Rack	8	
ii.	Weigh Tube	8	
iii.	Uncap Tube	16	
iv.	Add Acid	8	
v.	Weigh Tube	8	
vi.	Cap Tube	16	
vii.	Load Shaker	8	
viii.	Agitate Sample		0.5 hr.
ix.	Unload Shaker	8	
x.	Uncap Tube	17	
xi.	Add Solvent	8	
xii.	Weigh Tube	8	
xiii.	Cap Tube	16	
xiv.	Load Shaker	8	
xv.	Extract Sample		1.0 hr.
xvi.	Unload Shaker	8	
xvii.	Load and Balance Centrifuge	26	

xviii.	Centrifuge Sample		0.033 hr.
xvix.	Unload and Balance Centrifuge	26	
xx.	Uncap Tube	16	
xxi.	Weigh Tube	8	
xxii.	Pipette Solvent Quantitatively	45	
xxiii.	Repeat (xi - xxii)	169	
xxiv.	Pipette One Gram Equivalent	18	
xxv.	Aspirate Tubes	6	
xxvi.	Cap Sample Tube	16	
xxvii.	Return Tube to Sample Rack	8	
Total # Robotic Moves		**483**	**2.56 hr. (non Robotic Time)**

Since the time per Robotic Move is 30 sec., therefore Robotic Time = 1,449 sec. = 24.15 min.

Since by definition the rate limiting element in an application is the greater of the robotic time or the analysis time, the robotic time is the rate limiting element. However, since the times are distributed as follows:

Total Robotic Time = 24.15 minutes
Analysis Time = 0
Digestion Time = 30 minutes
Extraction Time = 60 minutes

This does not lead to a straight forward serialization, due mostly to the long extraction times. Hence, time balancing of the procedure must be employed where the rate limiting time is found which is an even divisor into all times.

This involves building idle time into the system:

Total Robotic Time = 24.15 minutes
Analysis Time = 0
Digestive Time = 30 minutes
Extraction Time = 60 minutes
Idle Time = 5.85 minutes

Now the Sample Output Rate can be calculated where:

Sample Output Rate = # samples that can be processed/hour
= 60/RLE (in minutes)
= 60/30 = 2 samples/hr.
= 48 samples/day.

7.0 FUTURE EXTENSIONS

i. The extension of this application to the clean up and analysis stages. Preliminary considerations show that extraction columbs to selectively bind the organics in question may be used to bypass Fluorasil cleanup.

ii. Due to the highly modular design of both hardware and software, this method may be modified with relative ease to other applications of similar scope. Once table layout for additional work stations required by a new application is performed software modification to drive the new method could be implemented and tested. Then the P.C. would contain a library of low-level routines, that could be called from any new application program.

APPENDIX A

5.3. Extraction Procedure - Fish

Most samples arrive for analysis as frozen foil wrapped fillets. Treat large whole fish individually. Wash off adhering mucous and pat dry with paper towel. Measure length to 0.1 cm and weigh to 0.1 g. Cut fish posteriorly along dorsal surface using stainless steel knife. Note sex. Strip epaxial musculature (the muscle above lateral line) from skin and place about 50 g in stainless steel cup and grind for 2 minutes with mechanical homogenizer (Virtis). Using a stainless steel spatula, transfer to aluminum foil cup, cover and designate laboratory number. Store in freezer (-40°C) until analysis.

In the case of small fish, such as minnows, the whole fish is homogenized. Smelt are headed, tailed, gutted and ground.

5.3.1. Using stainless steel spatula mix previously ground fish tissue in aluminum foil cup, to ensure homogeniety. Frozen samples should first be thawed for 3-4 hours.

5.3.2. Weigh 5 gm (± 0.1 gm) of sample into a previously tared centrifuge tube and record sample number and exact weight.

5 gm is the optimum sample size, smaller samples to a limit of 1 gm can be used when necessary. Maximum sample size is 7 gm.

5.3.3. Add 40 ml of concentrated Hydrochloric acid to the fish tissue in the tube and seal using teflon lined cap.

5.3.4. Affix tubes to rotary making tumbler ensure caps are securely sealed.

5.3.5. Operate tumbler at 30-45 rpm for 1 hour to ensure good dissolution of tissues.

5.3.6. Remove tubes from tumbler and add 25 ml 25% dichloromethane in Hexane (v/v). Replace caps securely.

5.3.7. Replace tubes on tumbler and extract at 30-45 rpm for 1 hour. Let stand if emulsion develops.

5.3.8. Remove upper solvent layer using pasteur pipette and bulb and transfer to erlenmeyer flask.

5.3.9. Repeat 5.3.6 - 5.3.8 with a second 25 ml 25% methylene chloride in Hexane (v/v).

5.3.10. Dilute acid layer voluminously with water and discard in suitable manner.

5.3.11. Add 1 - 2 gm powdered $NaHCO_3$ to erlenmeyer containing combined extracts and swirl gently to ensure neutralization.

5.3.12. Quantitatively transfer sample extracts from 125 ml erlenmeyer flask to a 100 ml volumetric using a filter funnel, glass fibre filter paper and sodium sulphate. Do not make sample up to the 100 ml mark until ready for cleanup.

5.3.13. Stopper flasks and store in appropriate cool, dark area for separation/cleanup.

Samples stored in this manner must be processed through cleanup and separation steps within 24 hours or irreversible precipitation of lipid and protein in the extract may occur and affect final analytical results.

5.3.14. Rinse all used glassware under running tap water then with reagent acetone and place in dishwasher or appropriate surfactant detergent bath.

5.4. Clean-up Procedure - Fish

The cleanup procedure used for fish, eliminates unwanted contaminants including lipids and the elution sequence used separates pesticides into three groups. In this procedure PCB's are separated (approximately 95% efficiency) from the DDT's in one step thus eliminating the need for further chromatographic techniques.

5.4.1. Make 100 ml volumetric flasks containing sample extract up to the mark. Pipette an aliquot containing equivalent of 1 g fish tissue (usually 20 ml) from volumetric flask. Transfer to graduated test tube and evaporate to oil residue on a Vortex evaporator. Add 1 ml hexanes.

NOTE: The natural oil in the sample acts as a keeper and allows this stage of evaporation to be taken to dryness (e.g. no solvent).

SECOND NOTE: The Florisil column described will handle up to 80 mg of oil. If the oil residue after evaporation is more than 0.1 ml, a volumetric dilution or alternate aliquot is required to decrease oil to within the 80 mg limit.

5.4.2. Assemble chromatographic columns by inserting Teflon plugs and a 0.5 cm glass wool plug in the bottom.

5.4.3. Remove Florisil from oven and pour enough to prepare 1 SPLIT CHECK COLUMN into a 100 ml beaker. Return Florisil bottle to oven.

5.4.4. Pour Florisil into column and tap gently to form a height of 24 cm.

5.4.5. Immediately apply split check sample (4.5.7.) in 1 ml hexanes to top of column.

NOTE: Split check comprised of waste fish extracts, fortified to 500 ng/ml op'DDT and 10 μg/ml PCB. (Aroclor 1254:1260 = 4:1).

5.4.6. Allow sample to drain just to top of column and add 1.5 ml hexane to top.

5.4.7. Continue adding hexane, 1.5 ml at a time until the entire column is wetted.

5.4.8. Place reservoir on top of chromatographic column. Add 30 ml hexane to reservoir.

5.4.9. Collect a first fraction of 18 ml from the column and then collect 6-10 separate 2 ml fractions. Label tubes with corresponding volumes contained.

5.4.10. All fractions are analyzed as in 5.8. This SPLIT CHECK is performed every day to allow for changes in the Florisil activity caused by humidity fluctuation. It must be done to ensure adequate PCB/DDT separation. Compare fractions to op'DDT standard. The split is taken at the first major appearance of op'DDT.

5.4.11. Remove Florisil from storage oven and pour enough for 4 columns (approximately 40 ml) into a 100 ml beaker and return Florisil bottle to oven.

5.4.12. Pour Florisil from beaker into columns while tamping column to form a 24 cm bed.

5.4.13. Place 50 ml centrifuge tube under each column.

5.4.14. Immediately apply the 1 ml sample extracts (5.4.1.) to the top of the columns using a Pasteur pipette and rubber bulb.

5.4.15. Allow sample to drain onto column until it reaches the top of the Florisil.

5.4.16. Rinse sample tube with two 0.5 ml aliquots of hexane and apply these to the column one at a time as above.

5.4.17. Add hexane 1.5 ml at a time until entire column is wetted.

5.4.18. Place reservoir on top of column and add 30 ml of hexane to reservoir.

5.4.19. Collect hexane in 50 ml centrifuge tube to the volume determined in the split check procedure. This is fraction A1.

5.4.20. Turn off stopcock and decant excess hexane off top of column into waste receptacle.

5.4.21. Remove any remaining hexane using Pasteur pipette.

5.4.22. Add 10 ml 25% v/v dichloromethane solution (reagent 4.5.3.). Place 15 ml centrifuge tube under each column.

5.4.23. Open stopcock and collect 15 ml. This is fraction A2.

5.4.24. Before solvent level reaches top of Florisil bed, remove fraction A2 tube, insert a 15 ml tube, add 10 ml 25% diethyl ether dichloromethane to reservoir. Collect all solvent until column stops dripping. This is fraction A3.

5.4.25. Add 2 ml iso-octane to each extract and insert fraction tubes in Buchler Vortex Evaporator as in 5.2.14 and evaporate to 2 ml.

NOTE: Do not let samples evaporate to dryness or serious pesticide losses occur.

5.4.26. Make up to 5 ml in iso-octane.

5.4.27. Analyze samples acording to 5.8.

FRACTION A1 contains:

PCB
HCB
Heptachlor
Octachlorostyrene
pp'DDE
Mirex
Aldrin

FRACTION A2 contains:

α BHC
γ BHC (Lindane)
β BHC
α Chlordane
γ Chlordane
o,p'-DDT
p,p'-DDD-
p,p'-DDT
Toxaphene

FRACTION A3 contains:

Oxychlordane
Heptachlor Epoxide
Thiodan I, II and Sulphate
Dieldrin
Endrin
DMDT

5.4.28. Rinse all used glassware under running warm water and rinse with reagent acetone. Place in dishwasher or appropriate surfactant detergent bath.

5.5. Extraction Procedure - Soils and Sediments (and Vegetation)

All sediment samples should arrive in the laboratory in solvent rinsed glass jars with foil-lined caps. Possible contamination causing unreliable results may arise from other containers. Although this procedure refers only to soils and sediment. Vegetation samples may also be analyzed according to this method by replacing the Sonifier extractor with a Polytron unit.

5.5.1. Determine water content of soil or sediment (see Moisture Determination section 5.7.).

5.5.2. Weigh appropriate amount (±.1 g) of wet sediment into 300 ml Berzelius Beaker to obtain 10 g dry weight (a maximum allowance of 5 g of water will limit amount of very wet sediments) and add 50 ml of acetone.

5.5.3. Extract by immersing Sonifier head in sample suspension and operating for 3 minutes. Disperse the heat generated by the homogenizer by cooling the beaker in an ice water bath during the extraction. The increase and decrease in vibration intensity should be gradual to prevent damage to the Sonifier. Rinse Sonifier head with 1-2 ml acetone. Let acetone drip into sample beaker.

5.5.4. Allow suspension to settle before filtering.

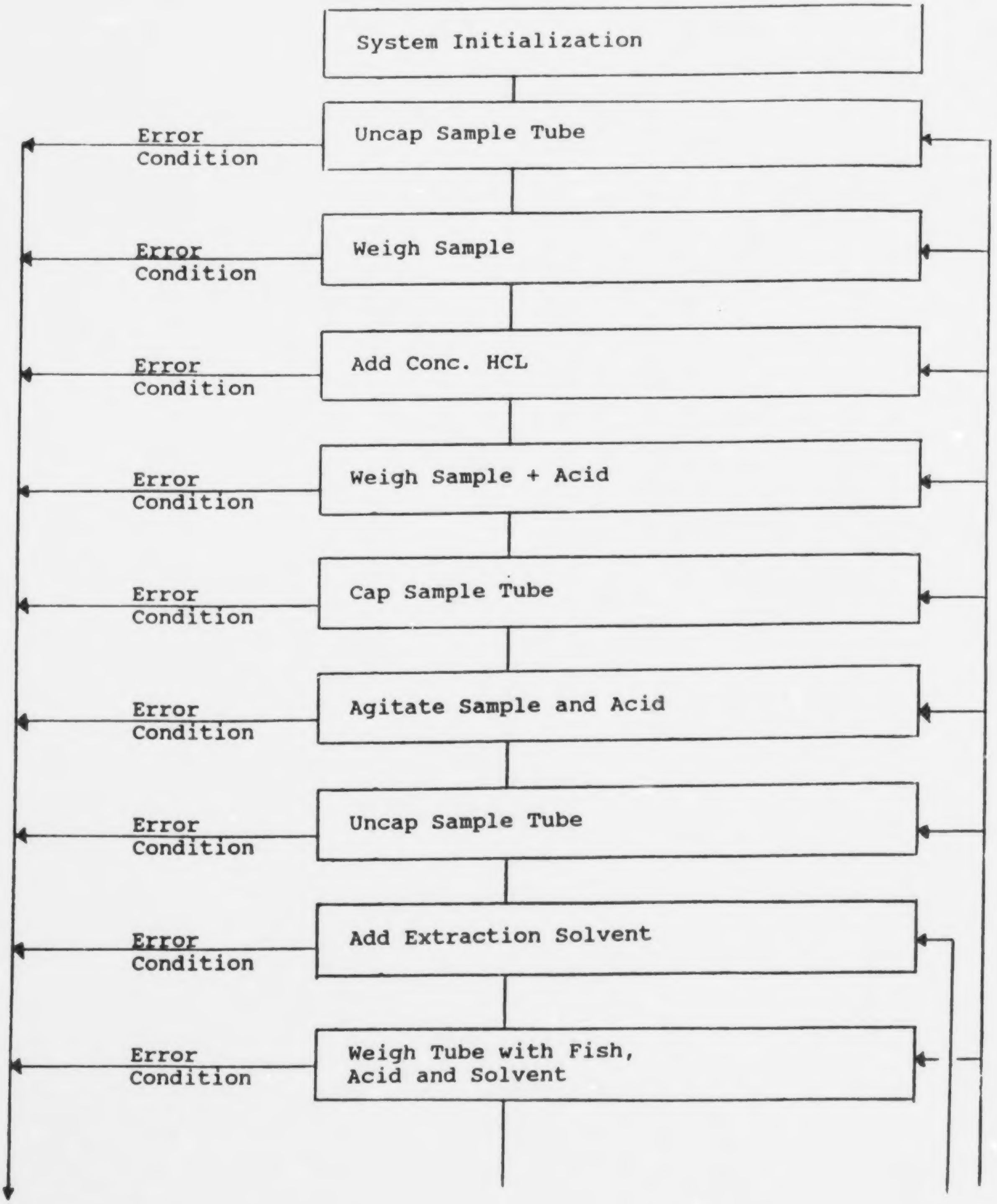
5.5.5. Insert a glass fibre filter and a 2 cm layer of Celite 545 onto the sintered disc of the Buchner funnel and rinse the whole assembly with 20-30 ml acetone. Discard rinsings.

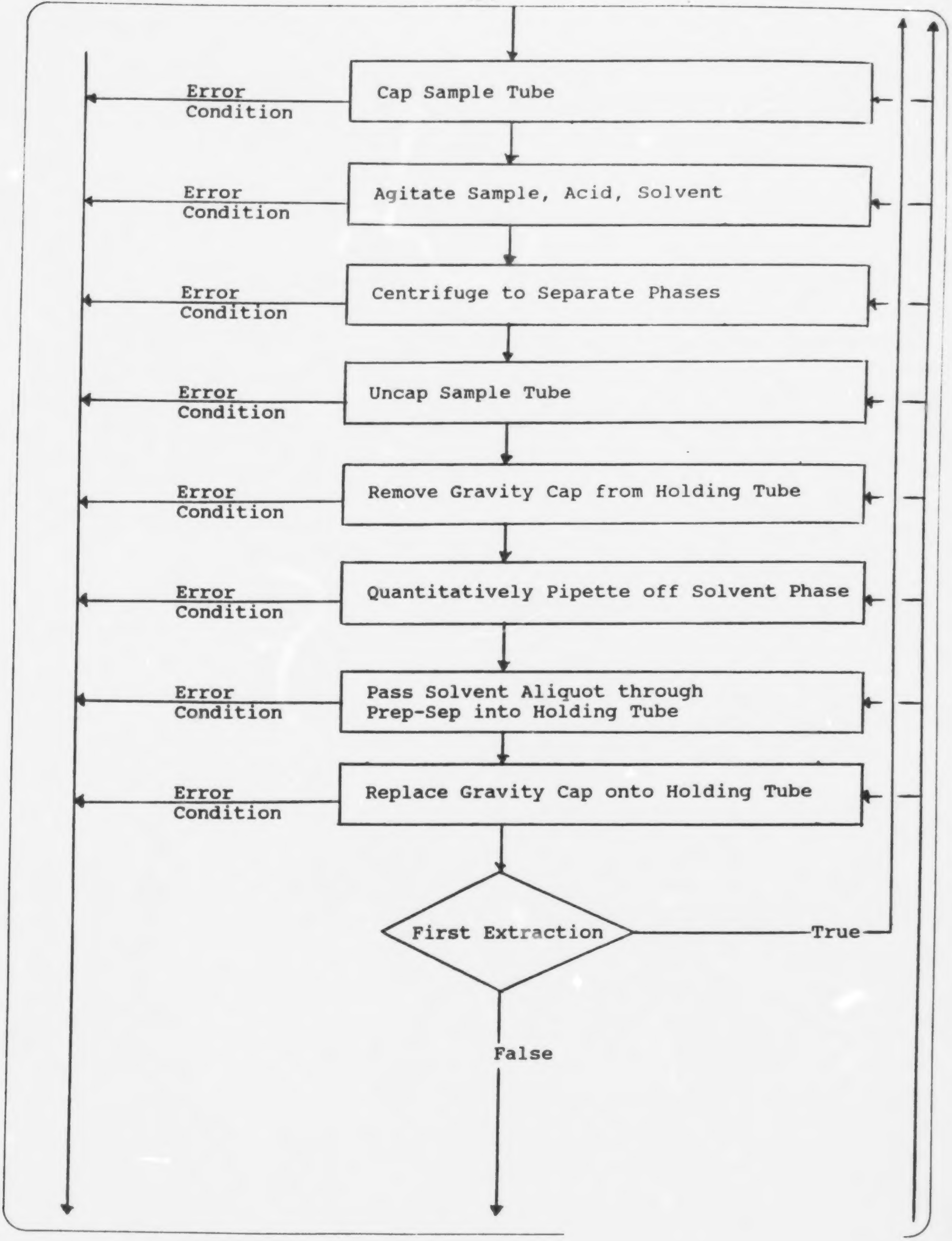
5.5.6. Filter sample supernatant through Buchner filter into cylindrical separatory funnel, with vacuum.

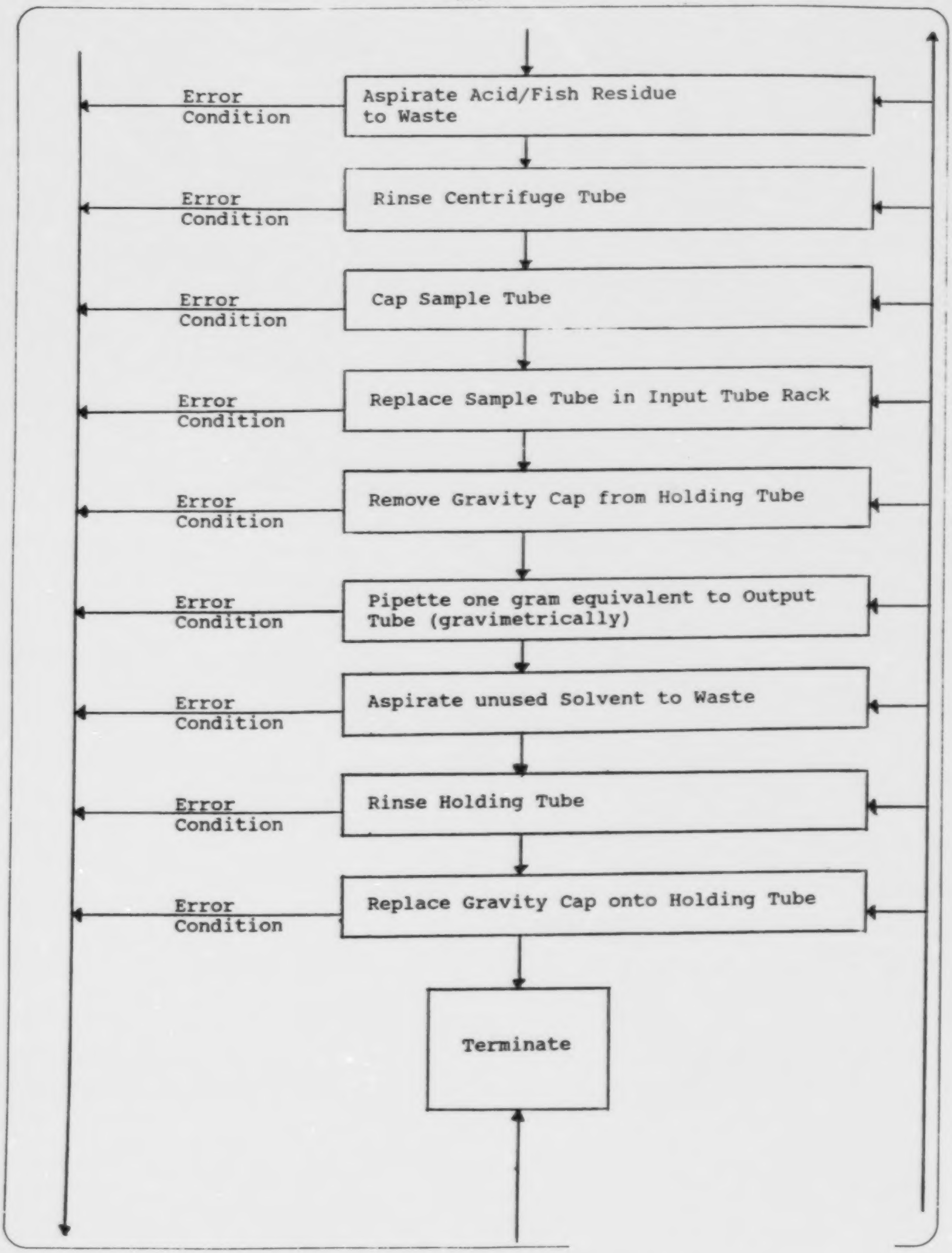
5.5.7. Add a further 50 ml acetone to remaining sediment and repeat extraction.

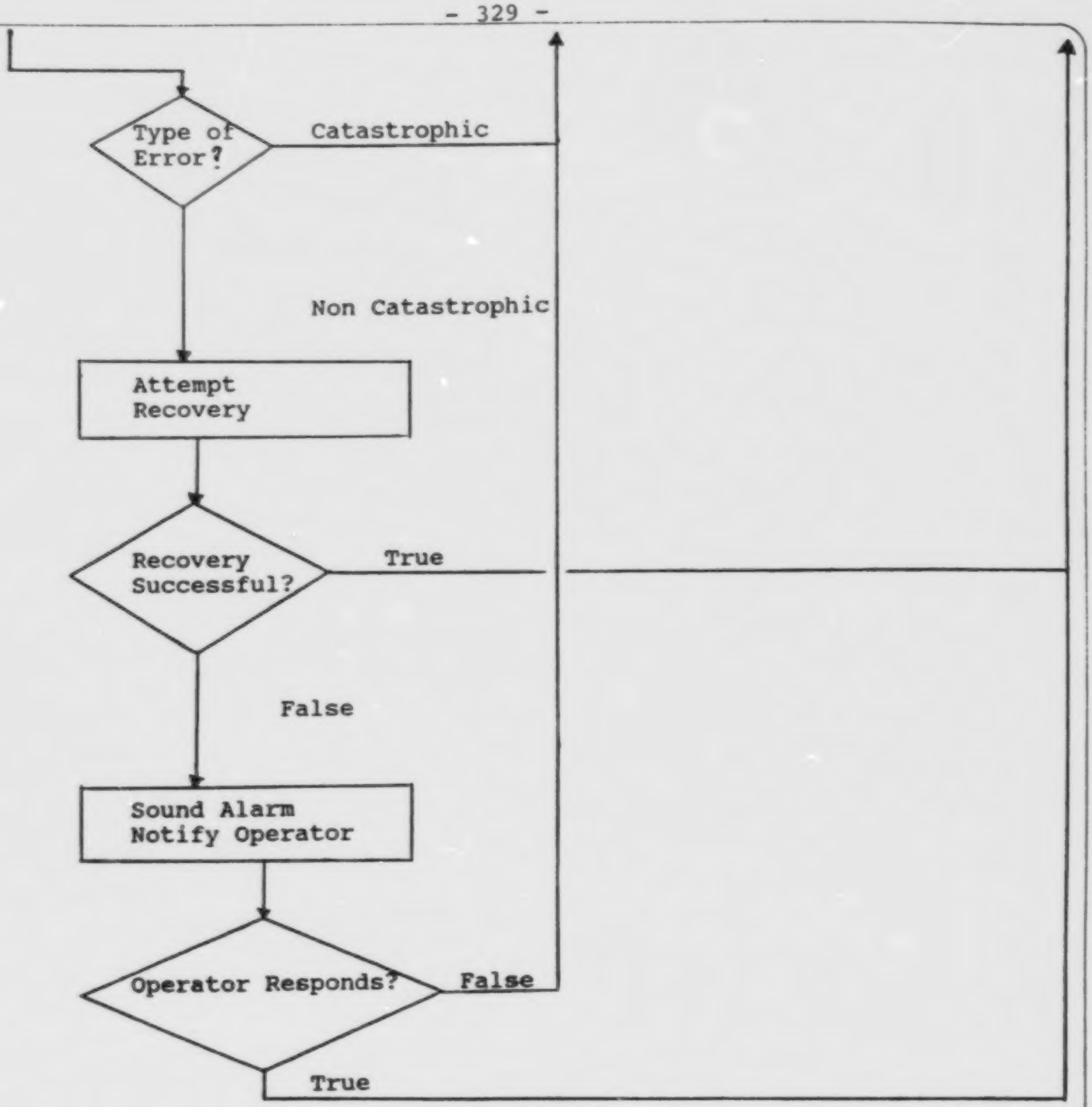
APPENDIX B

ACID DIGESTION/SOLVENT EXTRACTION FLOWCHART


System Initialization
Uncap Sample Tube
Error Condition
Weigh Sample
Error Condition
Add Conc. HCL
Error Condition
Weigh Sample + Acid
Error Condition
Cap Sample Tube
Error Condition
Agitate Sample and Acid
Error Condition
Uncap Sample Tube
Error Condition
Add Extraction Solvent
Error Condition
Weigh Tube with Fish, Acid and Solvent
Error Condition


Error Condition
Cap Sample Tube
Error Condition
Agitate Sample, Acid, Solvent
Error Condition
Centrifuge to Separate Phases
Error Condition
Uncap Sample Tube
Error Condition
Remove Gravity Cap from Holding Tube
Error Condition
Quantitatively Pipette off Solvent Phase
Error Condition
Pass Solvent Aliquot through Prep-Sep into Holding Tube
Error Condition
Replace Gravity Cap onto Holding Tube
First Extraction
True
False


Aspirate Acid/Fish Residue to Waste
Rinse Centrifuge Tube
Cap Sample Tube
Replace Sample Tube in Input Tube Rack
Remove Gravity Cap from Holding Tube
Pipette one gram equivalent to Output Tube (gravimetrically)
Aspirate unused Solvent to Waste
Rinse Holding Tube
Replace Gravity Cap onto Holding Tube
Terminate
Error Condition
Error Condition
Error Condition
Error Condition
Error Condition
Error Condition
Error Condition
Error Condition
Error Condition


Type of Error?
Catastrophic
Non Catastrophic
Attempt Recovery
Recovery Successful?
True
False
Sound Alarm Notify Operator
Operator Responds?
False
True

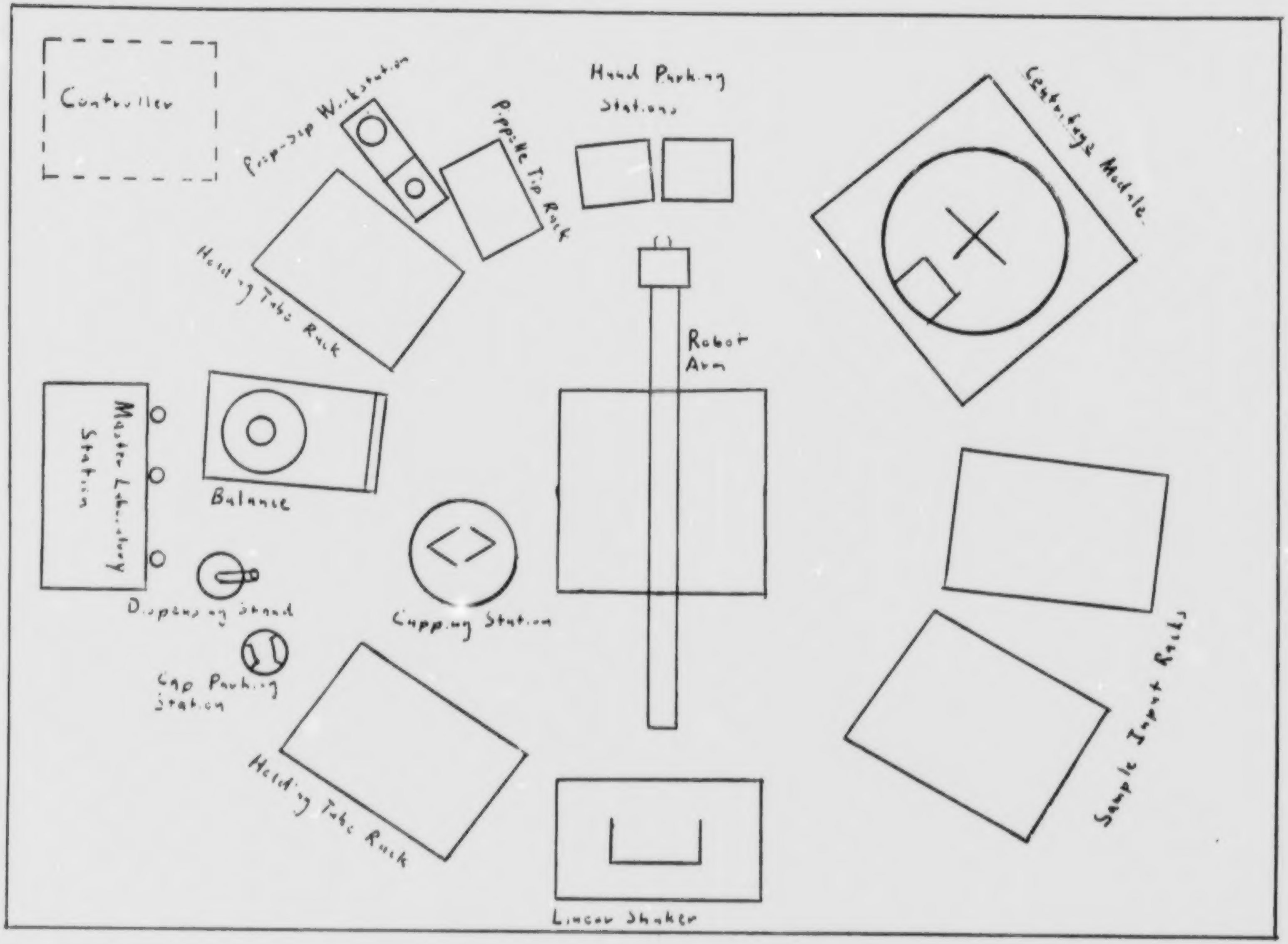

Controller
Pip-Dip Workstation
Pippette Tip Rack
Hand Parking Stations
Centrifuge Module
Holding Tube Rack
Robot Arm
Master Laboratory Station
Balance
Dispensing Stand
Capping Station
Cap Parking Station
Holding Tube Rack
Linear Shaker
Sample Input Racks

Figure I. Bench Layout

SEPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS IN AIR PARTICULATE EXTRACTS BY HPLC AND GC/MS

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ABSTRACT

The organic compounds in air particulate extracts were separated into acidic, basic, and neutral fractions by acid/base extraction. The neutral fraction consisted of a large number of aliphatic and aromatic compounds. The identification of aromatic compounds that co-eluted with other compounds was very difficult by gas chromatography alone. Semi-preprative high pressure liquid chromatography was used to separate aliphatic compounds into one fraction and the aromatic compounds in several subsequent fractions. The retention behavior of aromatic compounds on normal phase columns in high pressure liquid chromatography was found to be typical, where capacity factors increased with an increase in the number of rings and was not largely affected by the alkyl substitution or the position of alkyl substiution on a particular aromatic compound. The high resolution gas chromatography and mass spectrometry were used for compound identification. The advantages of acid-base extraction and high pressure liquid chromatography prior to GC-MS analysis are discussed in detail.

INTRODUCTION

The identification of organic compounds in ambient air have become increasingly important because of the presence of numerous toxic compounds. Many polynuclear compounds are on the Environmental Protection Agency (EPA) priority pollutants list because they are known or suspected to be mutagenic and/or carcinogenic (1). Previously, procedures using dimethyl sulfoxide and pentane for the separation of aliphatic and polynuclears in air particulate extracts have been reported (2). The various methods for the separation and identification of polynuclear aromatics in environmental and biological samples have been reviewed several times (3-8). Present instrumental methods with conventional detectors are not able to detect the traces of toxic pollutants directly in the air. Most of the work aimed at such an analysis involves collection of airborne particulate matter by high volume filtration techniques using glass fiber filters as collection media (9,10). The extraction of organic compounds from such filters and the extraction efficiency using various solvents is reported in the literature (11,12). The identification of a large number of compounds verlapping in gas chromatographic analysis is very difficult due to interference. These compounds can be separated applying different techniques based on their chemical properties. Acid/base extraction for the separation of compounds into acidic, basic, and neutral fractions has been reported in the literature (13). There has been a great upserge of interest in high performance liquid chromatography(HPLC) for the separation of various compounds based on their polarities. Semi-preparative HPLC has been used for the separation and isolation of various compounds into definite compound classes. An optimized HPLC program developed using standards can be used for the analysis of real samples because of the high reproducibility of HPLC method. Because of the high capacity and low efficiency of semi-preparative HPLC the identification of traces of compounds of interest is difficult by HPLC detectors. However, the HPLC fractions after concentration can be analysed very easily by capillary gas chromatography(GC). Thus, combination of more than one techniques for analysis of complex samples results in separation and identification of large number of compounds. We will report in this paper the use of acid/base extraction, semi-preparative HPLC, and gas chromatography mass spectrometry for the complete analysis of organic compounds in air particulate extracts. Samples were obtained from the Ontario Ministry of Environment, and were collected near a wood burning facility.

EXPERIMENTAL

Chemicals and Methods: The solvents used in this method were distilled in glass, UV grade from Caledon Laboratories, Ltd. (Georgetown, Ontario, Canada). The standard polyaromatic hydrocarbons (PAH) were purchased from Ultra Scientific, Inc. (Hope, RI) and Aldrich Chemical Company, Inc. (Milwaukee, USA). All the standards were prepared by dissolving 4 to 10 miligrams of each polyaromatic hydrocarbon in to an appropriate amount of benzene or mixture of benzene and dichloro methane and stored at below 0^0 C when not in the use.

The general scheme for the separation of organic compounds in air particulate extracts is shown in Figure 1. The air particulate extracts dissolved in toluene contained suspended particulate matter which was removed using a centrifuge. The compounds were then separated into three major groups, acidic, basic and neutral using the acid base extraction. The neutral organic compounds were further separated according to their polarities using HPLC.

Semi-preparative HPLC:

The separation and fraction isolation was achieved on a Varian 5000 Liquid Chromatograph with a

Vista 401 data system which has the capability to recalculate and replot the stored data of a particular analysis. A semi-preparative u bondapack (10 um) amine column (250 mm X 9.4 mm,I.D. Waters Scientific Ltd. Mississauga, Ontario, Canada) was used. The samples were injected by an automated Rheodyne injector with 100 ul sample loop. A gradient solvent program was developed for the separation of a standard mixture containing two to five ring PAH . The program consisted of 98 % hexane and 2 % dichloromethane for 12 minutes programed to 100 % dichloromethane at 45 minutes, held for 10 minutes and then linearly programmed to 100 % acetonitrile held for 10 minutes and then programmed back to 100 % dichloromethane and finally to hexane. The fractions were collected between 6 to 14, 20, 24, 28, 33, 37, 43, 55 and 80 minutes. All fractions were concentrated to 200 ul each for GC and GC/MS analysis.

GC Analysis:

The HPLC fractions were analyzed on a Hewlett Packard 5880 A GC equipped with flame ionization and electron capture detectors using a 30 m X 0.32 mm I.D. DB-5 fused silica capillary column (J and W Scientific, Inc., Rancho Cordova, CA, USA). The same column was used for the separation and characterization of individual compounds by GC/MS.

GC/MS Analysis:

GC/MS analysis was performed on a Hewlett Packard 5987 A with an HP 1000 data system which stores the raw data and permits drawing the mass spectra of any peak on the total ion current (TIC) trace. The library search system consists of probability based matching (PBM) based on 78,000 reference spectra. An ion source temperature at 200^0C was used the GC conditions were similar to those used in GC/FID analysis.

RESULTS AND DISCUSSION

It is very difficult to completely analyse the air perticulate extracts for organic compounds by GC alone because of peak overlap. The relative amounts of organic compounds in air particulate extract are varied and hence sample cleanup and concentration is necessary to remove interferences and to separate the compounds into different classes based on their properties such as acidity, basicity, polarity, volatility and structures using the different techniques prior to GC analysis. The general scheme for the separation of compounds into different classes is shown in Figure 1. The acid/base extraction is very important step to remove the water soluble inorganic impurities, and highly polar acidic and basic organic compounds from the neutral organics. From our experiments, we observed that the composition of the neutrals did not changed for a period of the several months. The probable reason for this stability might have been due to the removal of the catalytic inorganic impurities by the acid/base extraction. Such impurities can catalytically effect the changes in composition of untreated extracts (14). Similarly, we have observed that the GC column detoriate almost immeditely and peaks lose their symmetry if a sample without acid/base extraction was injected.

The neutral fraction after acid/base extraction consists mainly of aliphatic and aromatic compounds. The aliphatic compounds were highly concentrated and co-eluted with environmentally important polyaromatic compounds in GC analysis. The aliphatic compounds were separated from the aromatics using the normal phase HPLC. The reproducible separation of aliphatic compounds from aromatics was obtained on both silica and amine columns in HPLC. The gradient solvent program was optimized for HPLC using a mixture of standard PAHs. It was observed that the amine column is more selective than the silica column for the separation of PAH according to the number of rings. It was also observed that the best separation of aromatics having two and three rings can be obtained using nonpolar hexane for longer period of time or with higher flow rate. Prolonged application of hexane, however, results in peak broadening for the larger PAHs and they elute in more than one HPLC fraction. To overcome this difficulty the initial gradient program was modified from 100 % hexane to a composition of 98:2 hexane and dichloromethane used isocratically. Using this program it was observed that the PAH eluted faster where as the retention order remained the same. This program was used for the separation of neutral organics in various fractions.

In Figure 2, the UV trace, solvent gradient and flow gradient used for the analysis of organic neutrals by HPLC are shown. The fraction 1 (fig.3) exclusively consisted of aliphatic compounds. The majority of the GC peaks were identified by comparing the retention times of standards under identical conditions. The compounds identified are listed in Table 1. The peaks eluting after 45 minutes in Figure 3 are unsaturated aliphatic hydrocarbons identified by their mass spectra and a PBM library search.

The fraction 2 consisted of the two ring aromatics such as naphthalenes, biphenylenes and their alkyl substituents. These compounds are relatively highly volatile and hence their isolation and concentration without loss was very difficult. The peaks identified by PBM search are listed in Table II.

Fractions 3 and 4 mainly consisted of three ring PAH. It is seen from the Figures 4 and 5 that several compounds identified (Table II) have similar retention times using GC but can very well be separated by HPLC. For example 4H-Cyclopenta (def) phenanthrene exclusively eluted in HPLC fraction 3, while C_1-substituted three ring PAH with identical retention times on GC eluted in the HPLC fraction 4. Similarly naphthalene , 2-phenyl (Peak no.4 fig. 5) eluted in the HPLC fraction 4, the co-eluted compound by GC was separated only by HPLC. Several other peaks were also identified in fraction 3 that are not present in fraction 4 but have identical retentions on GC. The HPLC fractionation, therefore, resulted in the separation of a large number of compounds that would otherwise have identical retentions in GC analysis.

Fraction 5 consisted mainly of 4 ring PAH and is shown in Figure 6. All the peaks were identified by PBM search while fluranthene, pyrene, benzo(a)anthracene , triphenylene were confirmed by injecting the standard under identical conditions.

The retention behaviour of polar compounds is different than the aromatic hydrocarbons on the amine column in HPLC. Even though the three ring PAH eluted in fraction 3 , the three ring aromatics containing a carbonyl group were eluted in fraction 6 (fig.7). This indicated that amine column has a high selectivity to separate aromatic hydrocarbons according to the number of rings, where as the carbonyl substituted aromatics were retained very strongly. Fractions 7-9 do not show any peaks on GC/FID.

The highly polar and reactive (acidic) compounds isolated in the acid/base extraction and identified by GC/MS using the PBM search are reported in Table III (fig. 8). The acid/base extraction have two major advantages, one is to remove the inorganic impurities and the water soluble compounds that may be permanently retained on the HPLC column. The second is to sepatate the polar reactive organic compounds which otherwise require the application of very strong solvents and high flow rate for their elution from the HPLC amine column. The recoveries for selected PAH after acid base extraction were above 85 %. This indicates the simplicity and usefulness of an acid/base extraction prior to HPLC and GC/MS analysis.

CONCLUSION

A normal phase semi-preparative HPLC method using an amine column gave complete separation of aliphatics from aromatics and aromatics according to the number of rings. The complete analysis of environmental complex samples can be carried out using an acid/base extraction followed by HPLC and GC/MS analysis. This technique is very useful when the sample contains a large number of compounds having varied chemical and physical properties.

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TABLE I : Organic compounds identified in the HPLC fractions of air particulate extract.

Peak No.	Compound	RT (min)	Mol Wt.
Fraction 1 (Figure 3)			
1	Heptadecane	18.12	240
2	Octadecane	20.62	254
3	Nonadecane	23.23	268
4	Eicosane	25.74	282
5	Henecosane	28.10	296
6	Docosane	30.35	310
7	Tricosane	32.11	324
8	Tetracosane	34.59	338
9	Pentacosane	36.59	352
10	Hexacosane	38.53	366
11	Heptacosane	40.38	380
12	Octacosane	42.11	394
13	Nonacosane	43.96	408
14	unsaturated aliphatics		
Fraction 2			
1	Naphthalene, dimethyl	11.53	156
2	Naphthalene, dimethyl	12.48	156
3	Dibenzofuron	14.63	168
4	9H-Fluorene	16.49	166
5	9H-Fluorene, methyl	17.17	180
6	Dibenzofuran,methyl	17.61	182
7	Fluorene, methyl	19.69	180
8	Benzene,1-methyl-2-(2-phenyl-ethenyl)	22.79	194
9	9H-Fluorene, dimethyl	23.00	194
10	5H-Dibenzo(a,d)cycloheptene, 5-methylene	23.97	204
11	Naphthelene,1-(phenylmethyl)	26.88	218
12	Benz(a)anthracene,1,4,7,12-tetrahydro-	29.28	232

Table 1. Organic cmpounds identified in the HPLC fractions of air particulate extract (continued...)

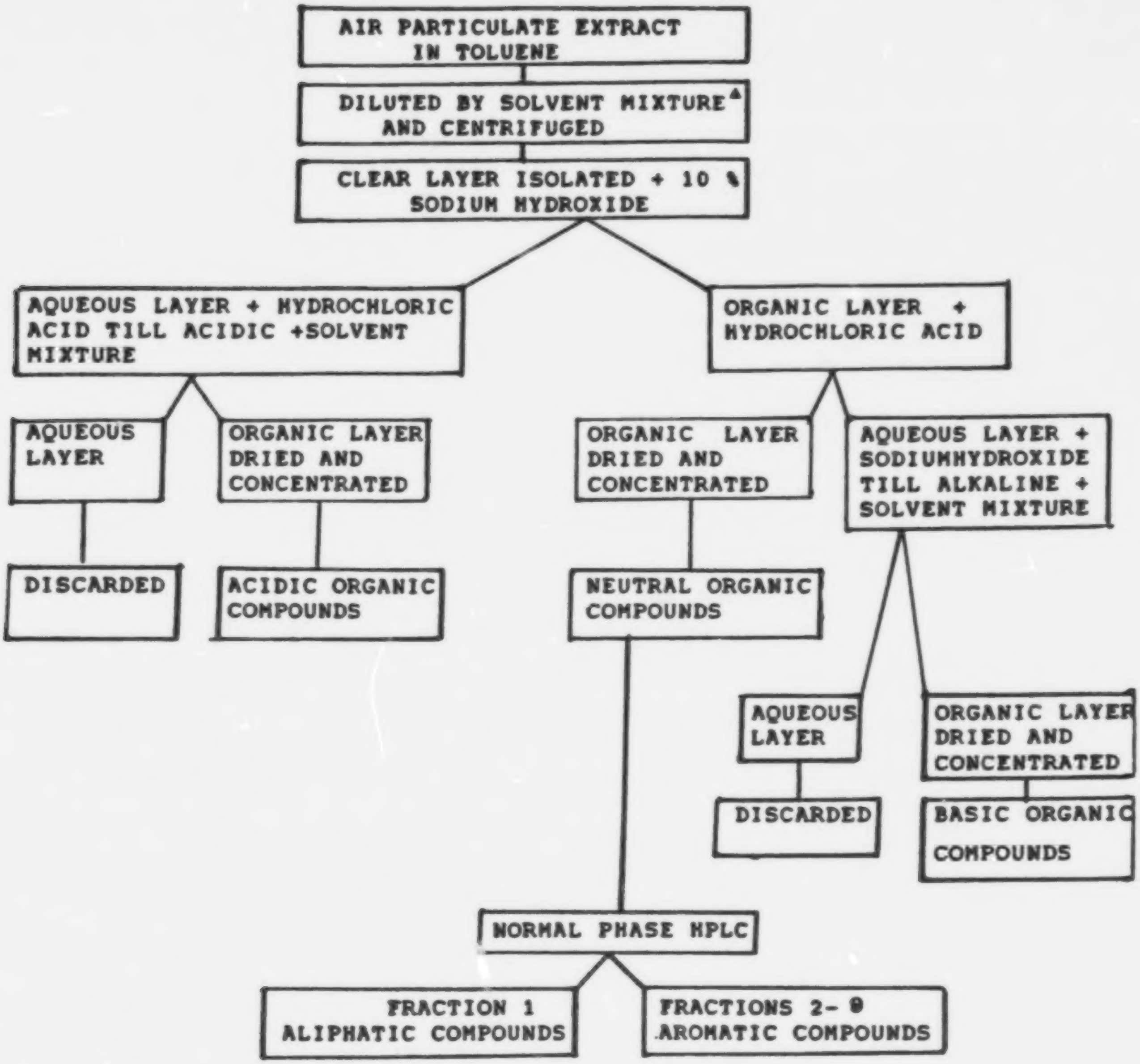
Peak no	Compound	RT (min)	Mol.Wt.
Fraction 3 (Figure 4)			
1	Phenanthrene	23.02	178
2	Anthracene	23.28	178
3(a-b)	C1-Substituted Phenanthrene/ Anthracene	24.00	192
4	1H-Indene,1-(phenylmethylene)	25.00	204
5(a-c)	C1-Substituted Phenanthrene/ Anthracene		192
6	4H-Cyclopenta(def)phenanthrene	24.46	190
7	C1-Substituted Phenanthrene/ Anthracene	27.04	192
8	Benzene 1,1'-(1-Cyclobutene-1,2-diyl)bis	28.00	206
9	Naphthylene, 2-phenyl	28.40	204
10(a-c)	C2-Substituted Phenanthrene/ Anthracene	29.85	206
11	Indenoindene	31.53	204
12	Pyrene,4,5-dihydro	31.96	204
13	Naphthalene,2 (phenylmethyl)	32.36	218
14	1,4-Naphthalenedion,5,8-dimethoxy	32.83	218
15	C3-Substituted Phenanthrene/ Anthracene	34.16	220
16(a-d)	Azulene,2,6-dimethyl-4-phenyl	36.39	332
Fraction 4 (Figure 5)			
1	Phenanthrene	23.06	178
2	Anthracene	23.30	178
3(a-d)	C1-Substituted Phenanthrene/ Anthracene	26.7	192
4	Naphthylene,2-phenyl	28.03	204
5(a-e)	C2-Substituted Phenanthrene/ Anthracene	28.98	206
6	Pyrene	30.96	202
7(a-c)	1,4-Naphthalenedion,5,8-dimethoxy	31.53	218
8	Disulphide,diphenyl	32.83	218
9	C1-Substituted Pyrene	34.16	216
10	Azulene,2,6-dimethyl 4-phenyl	34.51	232

Table 1. Organic cmpounds identified in the HPLC fractions of air particulate extract (continued...)

Peak no	Compound	RT (min)	Mol.Wt.
Fraction 5 (Figure 6)			
1	Fluoranthene	30.20	202
2	Aceaphenanthrene	30.75	202
3	Pyrene	31.19	202
4(a-e)	C1-Substituted Pyrene/11H-benzo(b)fluorene	33.05	216
5(a,b)	Chrysene/Triphenylene	35.05	228
6(a,b)	Benzo(ghi)fluoranthene	37.47	226
7(a-b)	Benzo(a)anthracene/chrysene/Triphenylene	38.74	228
8(a-c)	C1-Substituted Chrysene/Benz-(a)anthracene/Triphenylene	41.34	242
Fraction 6 (Figure 7)			
1	Furan, 2-butyltetrahydro	9.7	128
2	9H-Fluoren-9-one	22.17	180
3	1-Phenanthrenol	24.6	194
4	9(10H)- Anthacenone	26.2	194
5	9,10-Anthracenodion	28.3	208
6	Phenindione	31.6	222
7	7H-Benz(de)anthracene-7-one	36.8	230
8	Benzo(ghi)fluoranthene	37.69	226
9(a,b)	Chrycene/Triphenylene/Benz(a)anthracene	38.51	228
10(a-d)	Benzofluoranthene/Benzo(a)-pyrene/Benzo(b)pyrene/Perylene	44.92	252
11	Benz(j)aceanthrylene,3-methyl	46.80	252
12	1,2:3,4-Dibenzoanthracene	48.94	278
13(a-d)	1,2-Benzoperylene/Benzo(ghi)-perylene/Dibenzo(def,mono)-chrysene	51.81	276
14	Dibenzo(A,K)pyrene	57.84	302
15	Coronene	58.16	300
16	unknown	59.19	300

TABLE 2 : Acidic compounds identified in air prticulate extract (Figure 8).

Peak No.	Compound	RT	Mol Wt.
1	Phenol, 4-ethyl-2methoxy	6.78	152
2	Phenol,2,6-dimethoxy	8.88	154
3	Benzoic acid,4-hydroxy-3-methoxy-	11.36	168
4	2-Naphthalenol	12.98	144
5	Ethanone,1-(2,6-dihydroxy-4-methoxyphenyl)-	13.76	182
6	1-Naphthalenol, 4-methyl	16.06	158
7	(1,1'-Biphenyl)-3-ol	18.66	170
8	Unknown	22.68	182
9	Methanone,(2-hydroxyphenyl) phenyl-	25.50	198
10	Phenanthrenol	28.96	194
11	Phenol,2,6-dichloro-4-(1-methylpropyl)-	34.42	


AIR PARTICULATE EXTRACT IN TOLUENE
DILUTED BY SOLVENT MIXTURE▲ AND CENTRIFUGED
CLEAR LAYER ISOLATED + 10 % SODIUM HYDROXIDE
AQUEOUS LAYER + HYDROCHLORIC ACID TILL ACIDIC +SOLVENT MIXTURE
ORGANIC LAYER + HYDROCHLORIC ACID
AQUEOUS LAYER
ORGANIC LAYER DRIED AND CONCENTRATED
ORGANIC LAYER DRIED AND CONCENTRATED
AQUEOUS LAYER + SODIUMHYDROXIDE TILL ALKALINE + SOLVENT MIXTURE
DISCARDED
ACIDIC ORGANIC COMPOUNDS
NEUTRAL ORGANIC COMPOUNDS
AQUEOUS LAYER
ORGANIC LAYER DRIED AND CONCENTRATED
DISCARDED
BASIC ORGANIC COMPOUNDS
NORMAL PHASE HPLC
FRACTION 1 ALIPHATIC COMPOUNDS
FRACTIONS 2- 9 AROMATIC COMPOUNDS

▲ 20% DICHLOROMETHANE IN BENZENE

Figure 1. General scheme for the separation of organic compounds in air particulate extract.

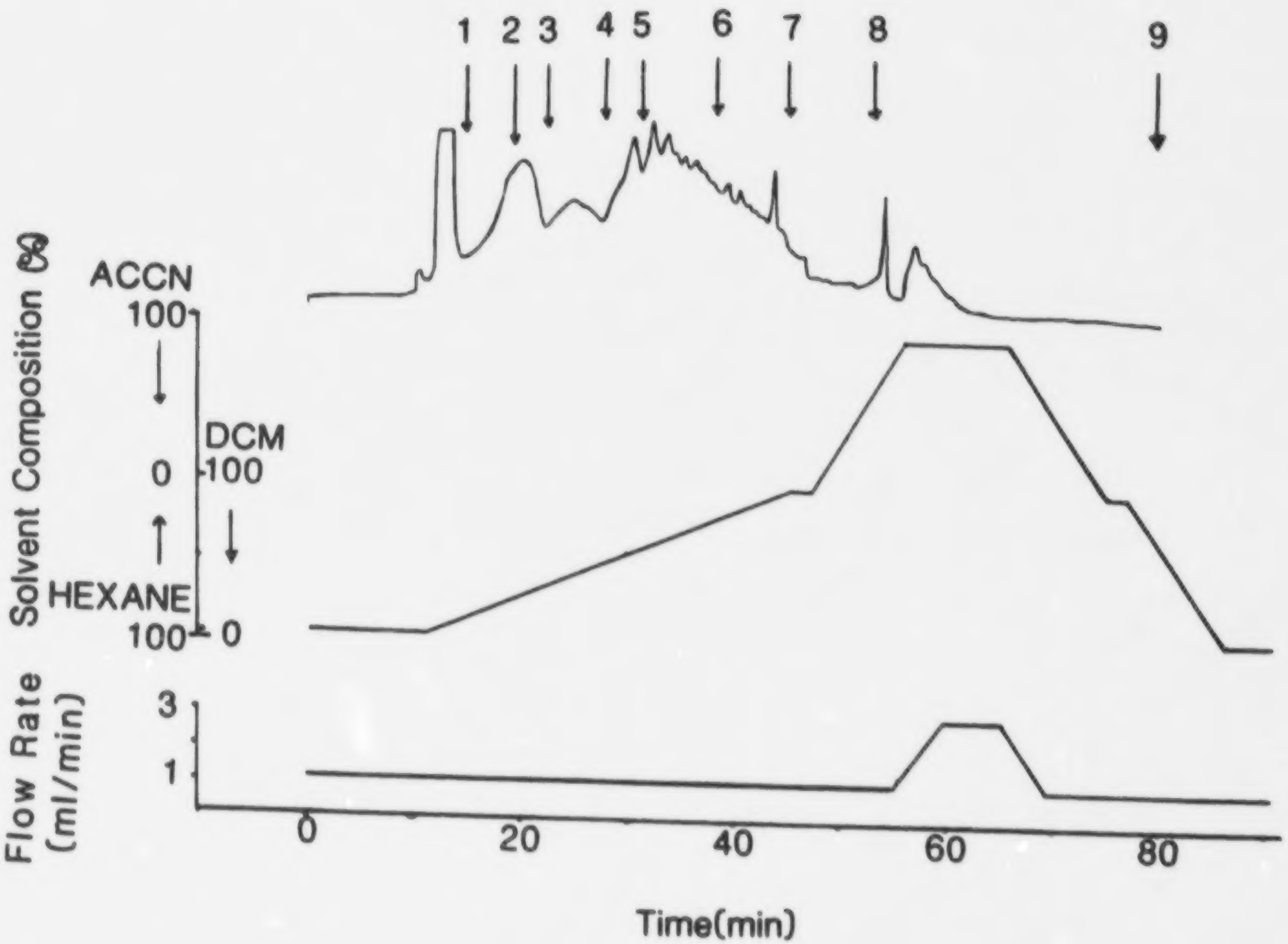


Figure 2. Scheme of the HPLC separation of neutral fraction of organics. a. UV trace in HPLC analysis, b. solvent gradient, and 3. flow gradient. Other conditions described in experimental section.

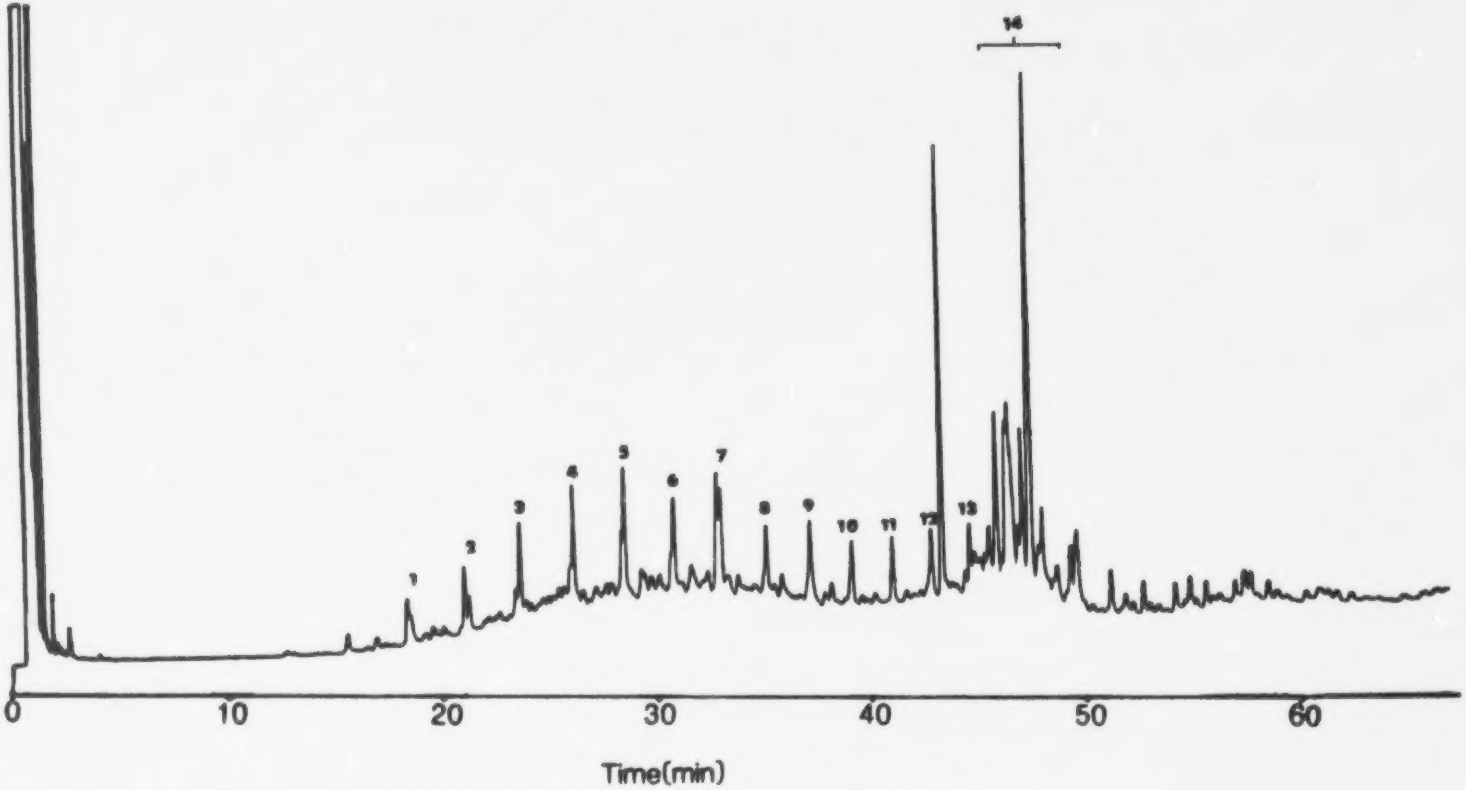


Figure 3. Gas chromatogram of HPLC fraction 1 of air particulate extract. Chromatogrphic conditions: 30 m X o.32 mm I.D., DB-5 fused silica capillary column; temperature, 80 ^{0}C for 1 min, programmed to 300 ^{0}C at 4 ^{0}C/min, 20 min at 300 ^{0}C, detector FID, peaks in Table 1.

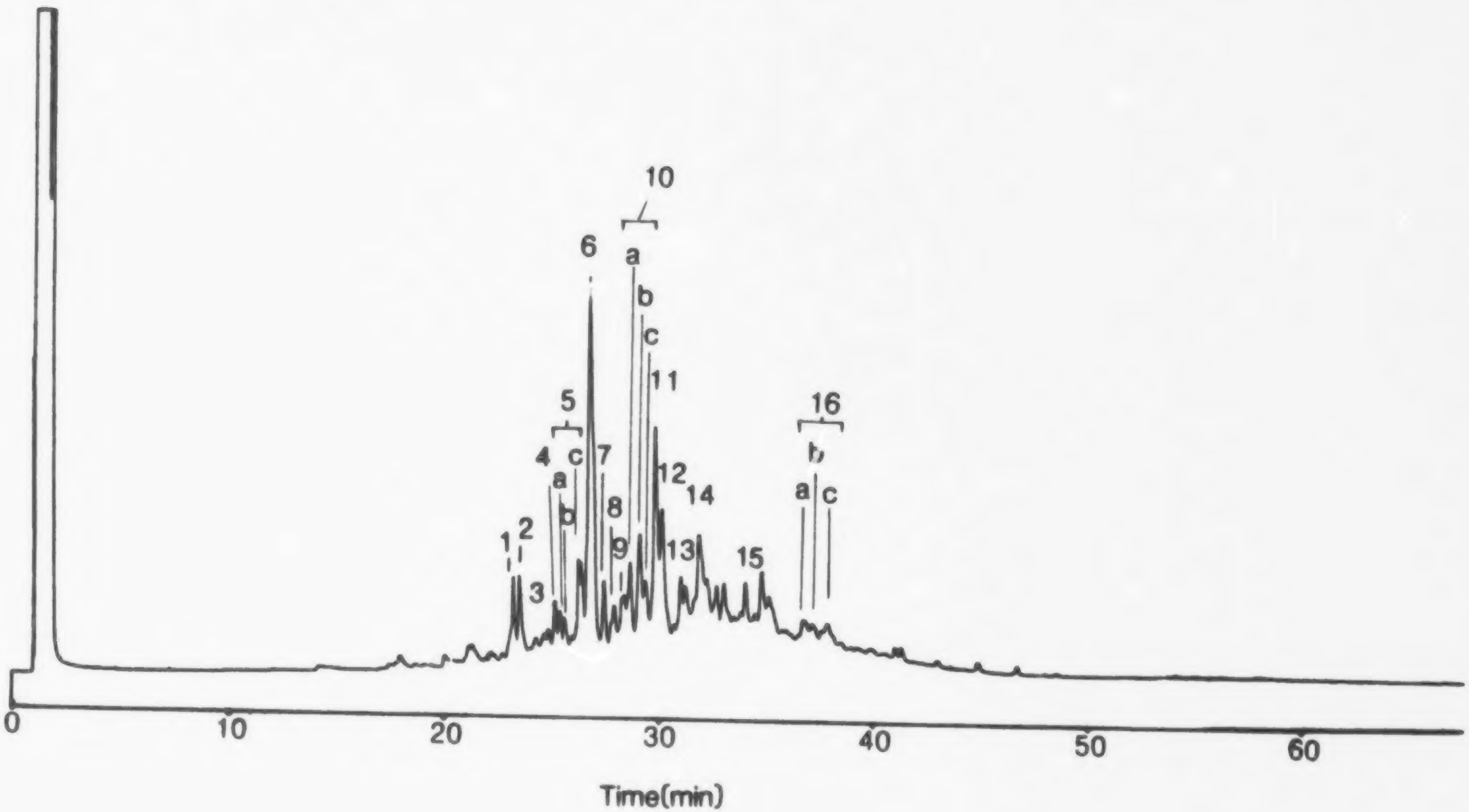


Figure 4. Gas chromatogram of HPLC fraction 3. Chromatographic conditions as in Figure 3. Peaks in Table 1.

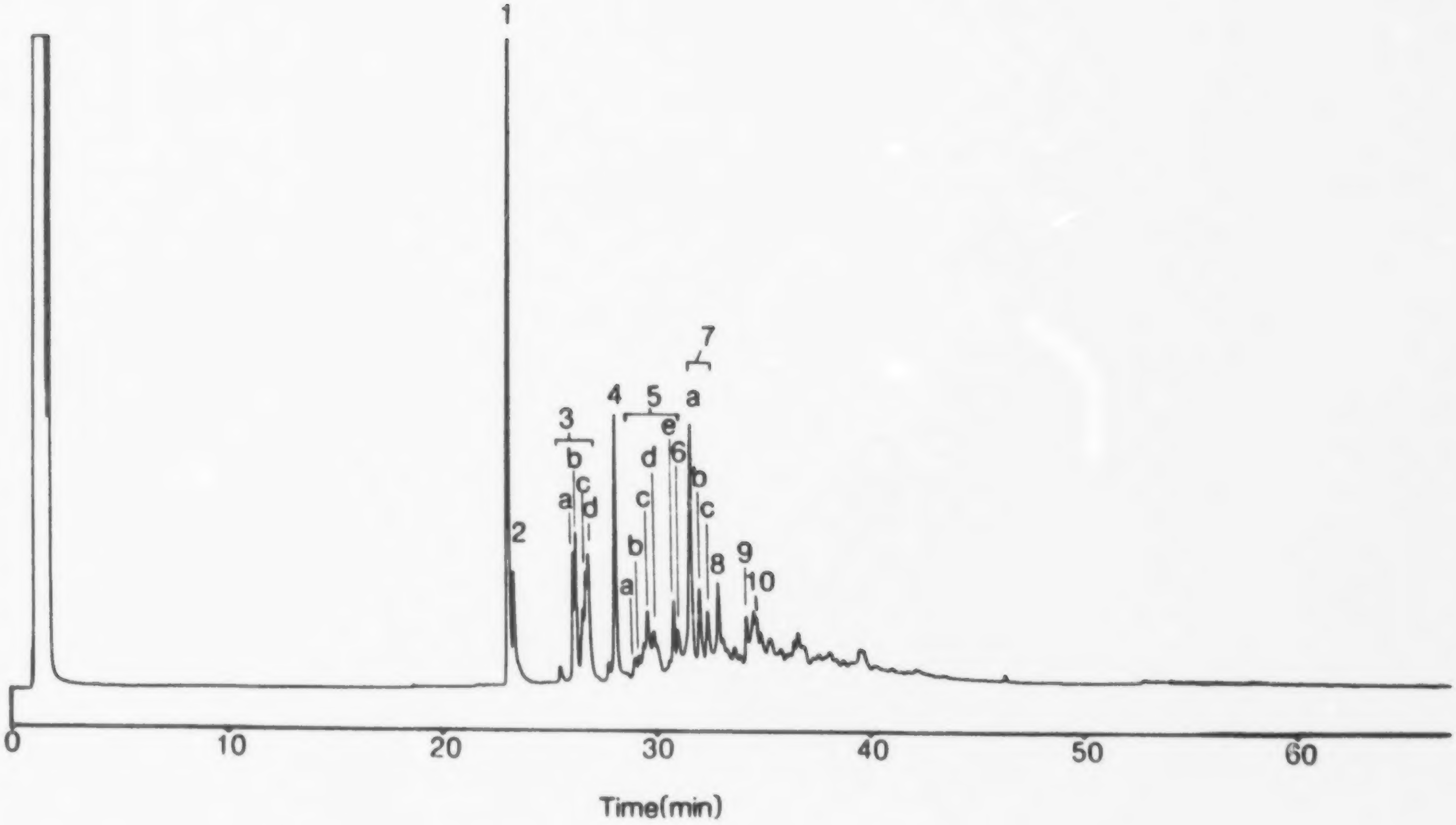


Figure 5. Gas chromatogram of HPLC fraction 4. Chromatographic conditions as in Figure 3. Peaks in Table 1.

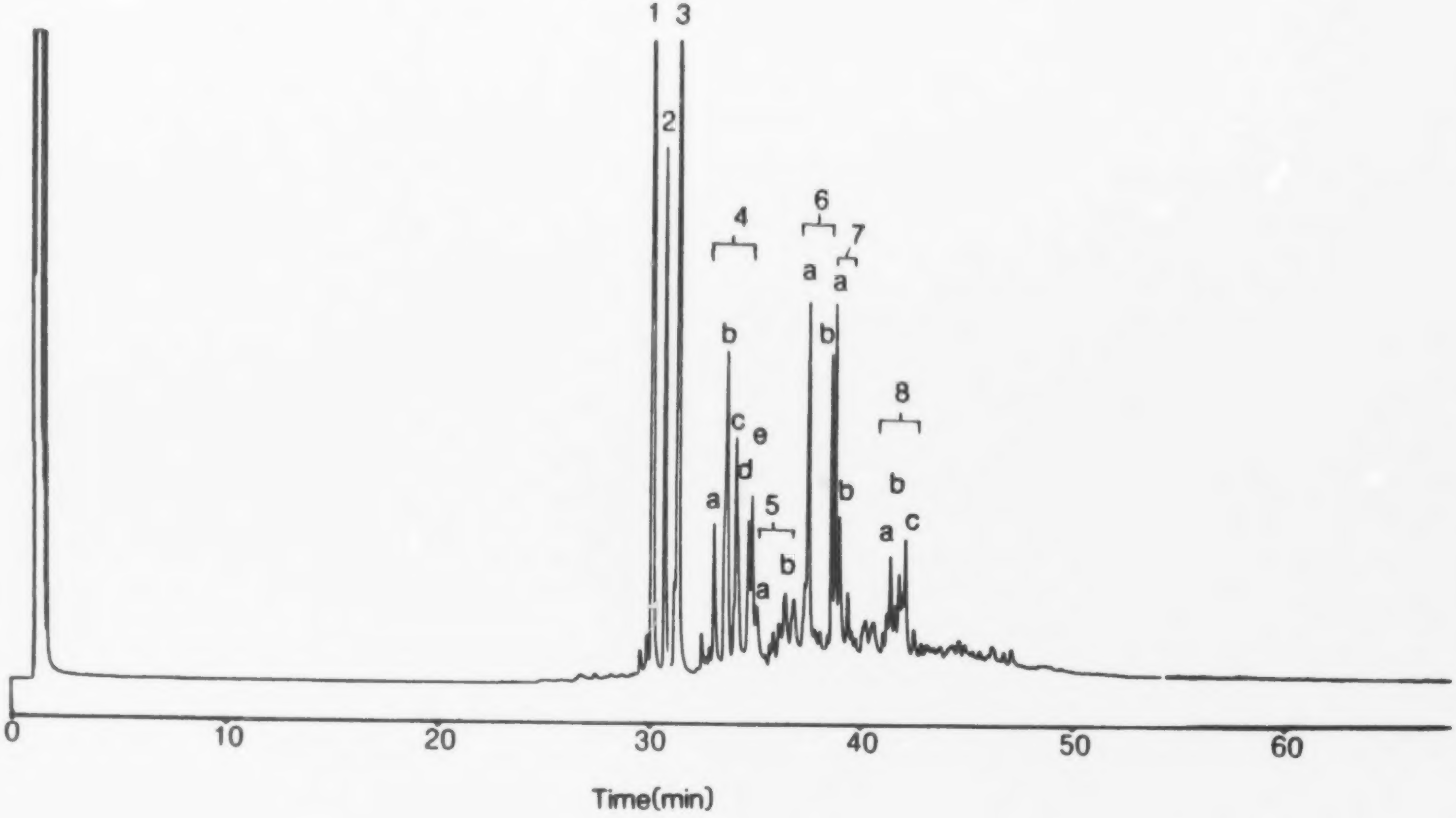


Figure 6. Gas chromatogram of HPLC fraction 5. Chromatographic conditions as in Figure 3. Peaks in Table 1.

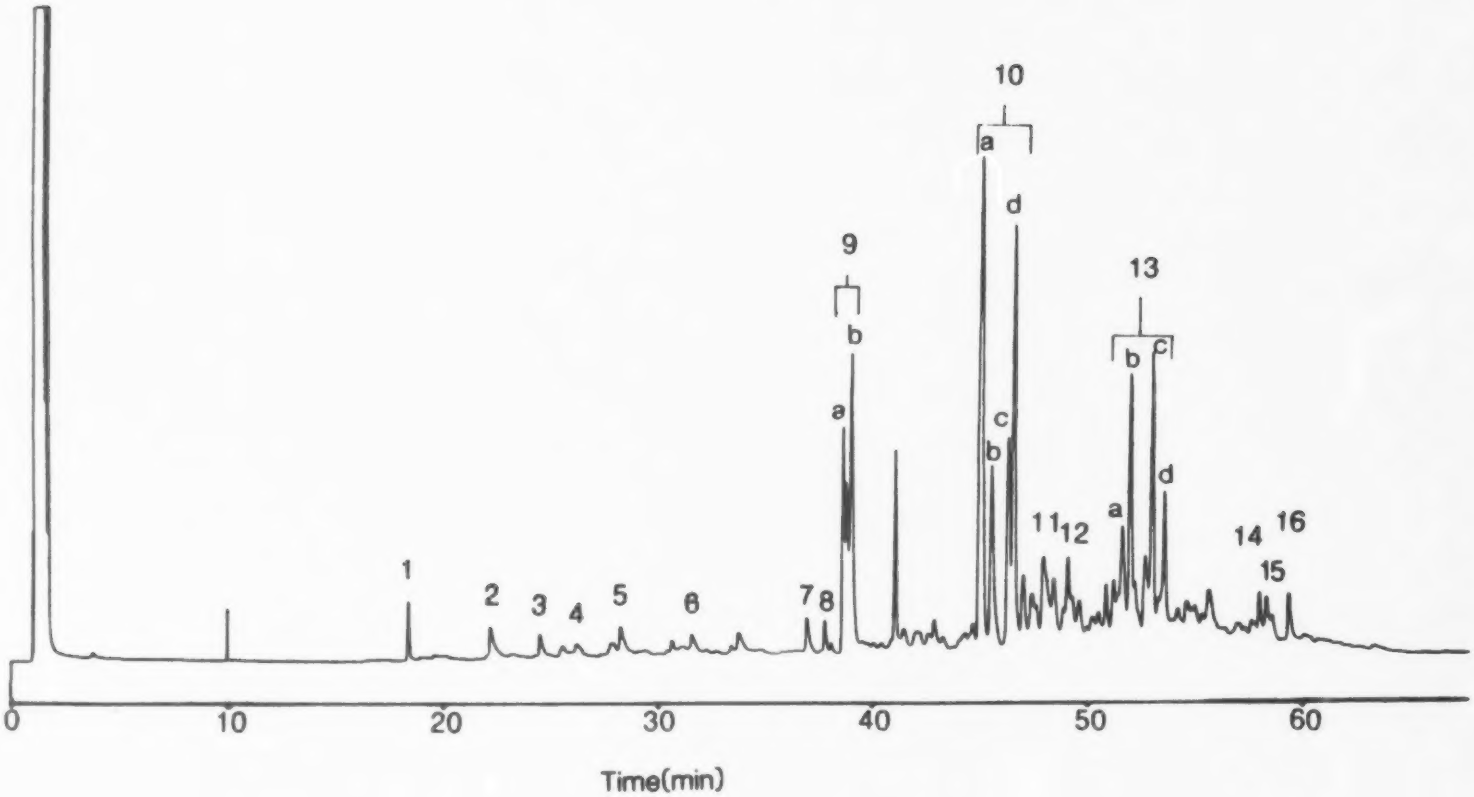


Figure 7. Gas chromatogram of HPLC fraction 6. Chromatographic conditions as in Figure 3. Peaks in Table 1.

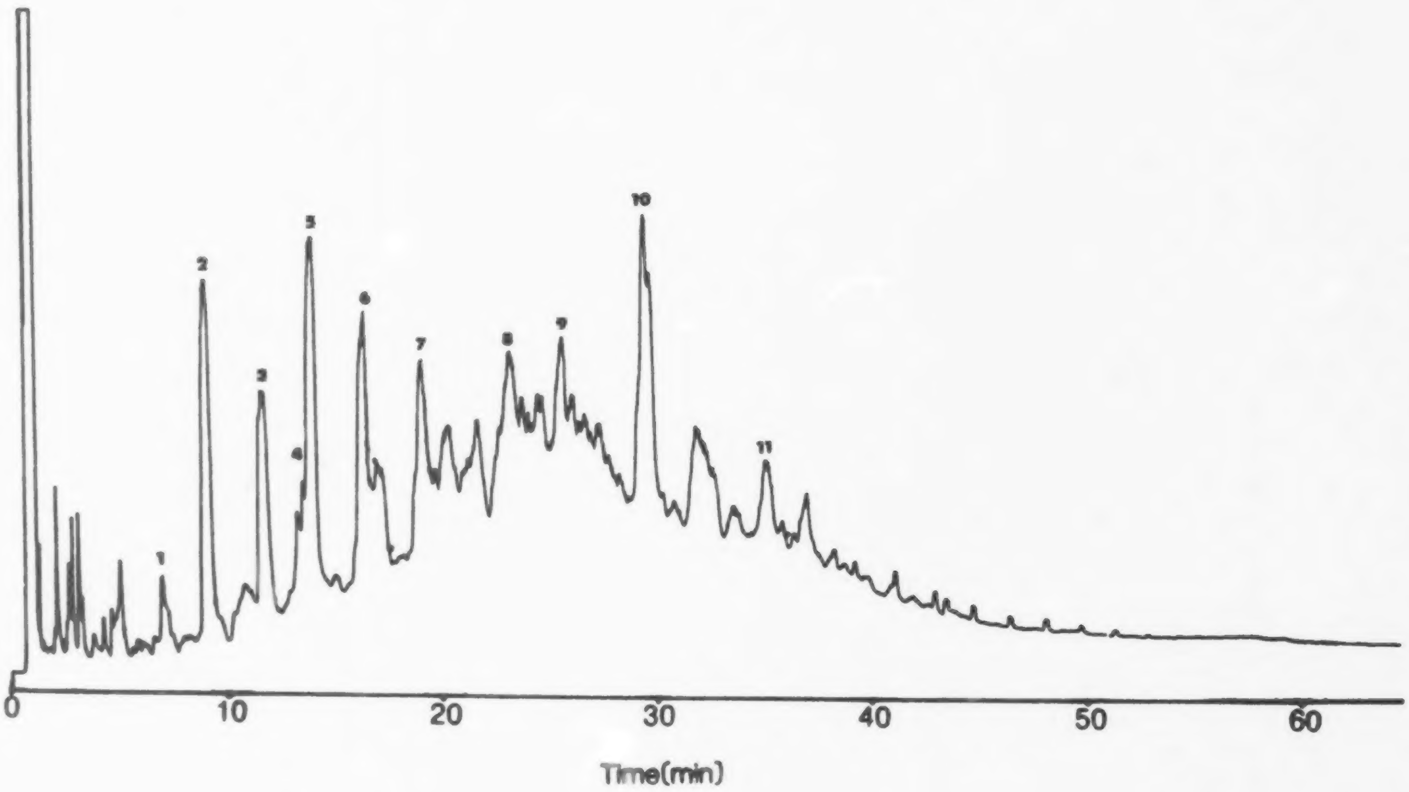


Figure 8. Gas chromatogram of acidic compounds separated by acid/base extraction. Gas chromatographic conditions as in Figure 3. Peaks in Table 2.

QUANTITATIVE DETERMINATION OF SELECTED PAH'S BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY

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1. Introduction

The case has been made over the last several years for the presence of trace quantities of PAH's in the environment, some of which have been demonstrated to be mammalian carcinogens and/or mutagens. Some problems, however, remain in current analytic techniques. Certain PAH's that are physical isomers of each other cannot be resolved by liquid chromatography. This becomes of importance when one or more of the isomers are carcinogenic. Optical spectroscopy techniques are, in principle, capable of differentiating between such isomers, since structural differences between isomers can lead to substantially different spectra. An example is provided by the laser excitation spectra of benzo(a)pyrene (carcinogenic) and benzo(e)pyrene (non-carcinogenic) in cold n-octane matrices obtained in our laboratory and seen in Figure 1. The use of tunable dye lasers as spectroscopic sources has other advantages besides the type of selectivity illustrated above. The high intrinsic intensity of a pulsed dye laser makes possible detection techniques of high sensitivity. In addition, the narrow laser linewidth (typically$<$ 0.1 nm.) allows one to separate closely spaced spectral features, and thus to minimize spectral interference effects arising from other species occurring in the sample being analysed. Further discrimination may be derived by taking advantage of varying radiative lifetimes of the component species in an environmental sample. For example, while perylene and benzo(a)pyrene, B(a)P, may potentially interfere with each other, this possibility can be reduced or eliminated by delaying observation of the laser induced fluorescence until, say 150 ns. after the laser pulse. Since B(a)P has a radiative lifetime of 270 ns. while perylene has a lifetime of 9 ns., it is easily seen that at a delay time of 150 ns. B(a)P fluorescence will still be strong, whereas perylene fluorescence will have become undetectible.

There are, however, severe problems associated with the spectroscopy of large molecules which must be overcome before spectroscopic techniques can be used to full advantage. The fluorescence and absorption spectra of large molecules consist generally of single broad, featureless peaks extending over 10 nm. or more. This is true whether the PAH is in the form of a solid or vapour, or dissolved in a suitable solvent. It is the high number of internal degrees of freedom coupled with the presence of many vibrational modes with small characteristic frequencies that is largely responsible for this state of affairs. The low values of PAH rotational constants exacerbates the problem. Even at room temperature many vibrational modes are excited, some possessing several quanta of energy, and rotational energy levels of high rotational quantum number are also prominent. Thus, even at room temperature the PAH molecule is characterised by a high density of occupied states and this must inevitably lead to a highly congested spectrum in which individual rotational lines cannot be resolved. Under certain conditions this problem can be overcome by cooling the PAH to very low temperatures, sufficiently low that only the lowest vibrational and rotational levels will be significantly populated. In our laboratory we use two methods, which will be described below.

One method makes use of a cryogenic refrigerator to cool the PAH and is the basis for the technique known as Shpol'skii spectroscopy by which, as will be explained below, it is possible to obtain discrete looking spectra of PAH's (1). However, merely cooling the solid PAH will not produce the desired simplification of the PAH spectrum. The PAH must first be dissolved in a suitable solvent and highly diluted. We normally use a heavy normal alkane, such as n-octane or n-hexane, as a solvent and dilute the solution to concentrations of 100 ng/mL or less. A small cell is filled with an aliquot, carefully dipped into liquid nitrogen for flash freezing and inserted into the refrigerator for further cooling to 20 K or less. The PAH molecule finding itself locked into a rigid matrix is now incapable of rotation, whereas the low ambient temperature ensures that only the lowest vibrational levels of the ground electronic state will be significantly occupied. The absorption of a resonant photon of appropriate energy will raise the molecule to an excited electronic state, which depending on the photon energy may also exhibit vibrational excitation. This excited electronic state may be either the first excited singlet or some higher state. Thus, as one scans the frequency of a laser through the absorption region of a specific PAH one will observe a number of sharp absorption peaks which measure the energy separations between the lowest lying vibrational states of the ground electronic state of the molecule and excited vibronic states. Normally, when using a laser as described above, one measures the fluorescence resulting from photon absorption by using either a monochromator set at a fixed wavelength or a suitable narrow bandpass filter rather than measuring laser beam attenuation. The resulting spectrum is called an excitation spectrum. The spectra shown in Figure 1 are examples of excitation spectra. The widths of the absorption features or quasi-lines of a given PAH are dependent on the temperature of the matrix, the nature of the solvent, the concentration of the solute and the technique used to first freeze and then further cool the sample. The linewidths decrease very rapidly with temperature to about 20K and then relatively slowly beyond 20K. At these low temperatures, widths of a few hundredths of a nanometre are typical. The solvent must be chosen carefully. Long chain normal alkanes are well suited to PAH's, because in their frozen matrices the PAH molecules are well aligned along the lengths of the solvent molecules and this minimizes without necessarily eliminating orientation effects. Concentrations must be chosen low enough to minimize solute-solute interactions. Flash freezing the solution in liquid nitrogen forms myriad micro-crystals and reduces the chances of forming a glass, which would produce relatively broad absorption features. Finally, not all solutes are capable of showing the Shpol'skii effect.

Another type of spectrum can also be obtained from matrix cooled PAH's by electronically exciting the PAH with a laser operated at a fixed resonant frequency and dispersing the resulting fluorescence with a scanned monochromator. Such a spectrum is called a fluorescence spectrum. Depending on the energy of the absorbed photon the electronically excited PAH may also be vibrationally excited. However, non-radiative relaxation will deactivate vibrationally excited molecules in the first excited singlet state to the lowest vibrational level of the state within the radiative lifetime of the excited electronic state. Molecules excited to higher electronic states are also removed to the lowest vibrational level of the first excited singlet state with like efficiency. One consequence of this is that fluorescence spectra are independent of the excitation wavelength. Another is that the quasi-line features of fluorescence spectra measure the energy separations of vibrational levels in the ground electronic state.

The second type of cooling used in our laboratory involves a supersonic jet. The PAH is maintained at a selected vapour pressure in the stagnation chamber by heating, an inert gas is admitted to the chamber and the mixture is expanded adiabatically through a pinhole into another chamber kept at a low background pressure by fast pumping. The pinhole is chosen large enough to exceed the limits for molecular flow, but small enough not to place inordinate demands on the pumping system. An overexpanded jet is formed in which the random molecular translational motion characterising the gas in the stagnation chamber is converted almost wholly into directed bulk flow. The translational temperature is thus reduced considerably and at 50 nozzle diameters downstream of the pinhole the temperature of a gas such as helium or argon would be less than 1K. Vibrational and rotational modes are being cooled at the same time, but with reduced efficiency. Because of the low vibrational and rotational constants of PAH's, these internal modes are also considered to be at low temperatures, which are perhaps higher than the local translational temperature, in a supersonic beam. Such a conclusion arises from the appearance of spectra obtained of beam cooled PAH's. Generally it is not practicable to determine vibrational and rotational temperatures of PAH's in supersonic beams. We have, however, measured a rotational temperature of about 6K for a NO_2 seeded argon beam at a distance of 50 nozzle diameters downstream of the pinhole. We are confident, therefore, that only the lowest rotational levels of the lowest vibrational levels of the ground electronic state of a given PAH molecule occur to any significant extent. If the laser linewidth exceeds the rotational spacing of a PAH, then the features in an excitation spectrum will represent individual vibrational bands of the electronic transition being probed and the widths of these bands will reflect the convolution of the rotational band profile and the laser line shape. In excitation spectra the observed bands measure the energy separations of individual vibrational levels of the excited electronic state and those populated in the ground electronic state. It is also possible to obtain fluorescence spectra of PAH's in cooled beams, but our experiments did not include such measurements and consequently such fluorescence spectra will not be discussed in this report.

There are similarities as well as differences between jet-cooled and Shpol'skii spectra. Since PAH molecules are essentially isolated and in a collision free environment, internal conversion is not an important process in supersonic beams. It is, however, of crucial importance in a frozen matrix. Consequently fluorescent spectra of PAH's in a jet beam are expected to be richer than in a frozen matrix since these are expected to show transitions from excited vibrational levels of the excited electronic state. In the frozen matrix the PAH-solvent interactions shift the energy levels of the PAH molecule whereas intermolecular interactions in the jet beam are essentially negligible. As a result, a given Shpol'skii feature occurs at longer wavelengths than the corresponding cooled beam feature. Another related feature in Shpol'skii spectra is the occurrence of multiplet structures arising from different orientations of the PAH within the matrix, an effect absent in cooled jet spectra. The width of a Shpol'skii quasi-line feature is determined mainly by photon interactions with the PAH whereas the width of a feature in a jet cooled spectrum of a PAH is determined by the rotational population distribution at the local rotational temperature.

We have previously reported our success in using the Shpol'skii technique to identify a number of priority PAH's in an environmental sample to the Sixth Tchnology Transfer Conference held in 1985. Our identifications were confirmed by HPLC analysis. In the present stage of the project we are extending our investigations to develop quantitative methods based on both the Shpol'skii and jet beam techniques. Although considerable progress has been made the work has not yet been completed and what will be presented here will be in the nature of a progress report which emphasises our work in cooled beams not reported previously.

2.0 Experimental Section

2.1 Jet-Cooled Spectroscopy

The beam chamber consists of a cubic stainless steel box measuring about 30 cm along one side and fitted with aluminium flanges. The laser beam is brought into the chamber and allowed to exit from the chamber by means of 0.5 m baffle arms to the ends of which are attached quartz windows mounted at the Brewster angle. The supersonic beam nozzle is mounted with its axis pointing at a right angle to the laser beam and intersecting it. The nozzle can be moved along its axis in order to vary the downstream distance at which the laser intersects the supersonic beam. The laser beam is focussed to a spot of approximately 1 mm in diameter to reduce the level of laser radiation scattered from the beam nozzle which is only 3 mm away from the intersection point of the two beams. The laser induced fluorescence is collected by a lens, focussed onto an aperture positioned to block both scattered light from the laser and window fluorescence and finally passed through a collection of filters onto the cathode of an EMI 6256 photomultiplier. The base of this photomultiplier has been wired to give the photomultiplier a linear signal response up to an anode current of about 1 ma. The beam chamber is maintained at a background pressure of about 0.3 mTorr, while the supersonic jet is operating, by a liquid nitrogen trapped 6" CVC oil diffusion pump. A large target made of stainless steel sheet material is positioned about 10 cm downstream of the nozzle orifice to trap any PAH's in the supersonic beam impinging on it. The collected material is washed into a storage bottle and disposed of in suitable fashion.

The optical probe pulse is provided by the oscillator stage of a Lambda-Physik FL2000 tunable dye laser, which was modified by replacing the telescope beam expander with one based on four quartz prisms. With this arrangement laser linewidths of about 0.01 nm are achievable; however, in our experiments we use a linewidth of 0.06 nm, which is sufficient for our purposes. The dye laser is pumped by a 3 mJ pulse from a Molectron nitrogen laser operated at a repetition rate of about 10 Hz. The laser wavelength is determined with the aid of a 1/3 m Heath monochromator. The dye laser energy is measured absolutely with a pyroelectric detector and relatively by either of two methods. In one method, a portion of the beam is removed with a microscope slide and viewed with a blue sensitive photodiode. In the second method, the monochromator is set at the wavelength of the PAH band being excited and the intensity of the laser beam at this wavelength is monitored with a RCA 1P28 photomultiplier at the exit slit. The wavelength of the laser beam is determined with the aid of a Heath 1/3m monochromator.

Initially a pulsed NRC BV-100 beam valve was used fitted with a 0.5 mm orifice; however, this valve could not be operated at the temperatures needed to generate useful vapour pressures of PAH's. Consequently a continuously operating beam nozzle was built as shown in Figure 2. Because of limitations imposed by our vacuum pumps we are required to limit the total throughput of gases into the beam chamber. The present orifice is 0.065 mm in diameter and we are obliged to keep the stagnation pressure, i.e. the total pressure of the gas on the high pressure side of the orifice, at a maximum of 200 Torr. This fortunately does not restrict the density of PAH molecules in the supersonic beam itself, since this is determined by the PAH vapour pressure maintained in the stagnation chamber and not by the total stagnation pressure. The beam nozzle is constructed of stainless steel to minimize heat conduction apart from the 4.2 cm section at the orifice end, which is constructed of copper for efficient distribution of heat. The copper end is wound with nichrome wire for the purpose of heating. The sample is placed into a small well at the end of a conical copper insert which is supported via a metal-to-glass seal by a 25 mm o.d. pyrex tube chosen to minimize heat conduction. A vacuum seal is effected by means of an O-ring between the pyrex tube and the stainless steel body of the beam nozzle. A chromel-alumel thermocouple attached to the copper insert is used to monitor the temperature of the sample. Pre-purified argon is added to the stagnation chamber without further purification and allowed to mix with the PAH vapour prior to passage into the beam chamber via the orifice. The stagnation pressure is measured with a Matheson absolute pressure gauge and is controlled only by the gas regulator attached directly to the argon tank.

The supersonic jet would be expected to have a roughly conical shape, if it were to expand into a perfect vacuum. However, collisions between beam molecules and the ambient molecules in the beam chamber form a standing shock wave which defines the limits of the beam. This shock moreover has a concave shape as seen from the beam axis and at some distance downstream of the nozzle causes the flow lines followed by the beam molecules to converge into a shock front, called a Mach disk, which is normal to the beam axis. Throughout the region between the nozzle and the Mach disk the beam molecules continue to be cooled. However, passage of these molecules through the Mach disk results in a compression that, in fact, increases the temperature and makes the Mach disk an unsuitable region for the type of spectroscopic measurements being carried out in the present study. Under our experimental conditions (stagnation pressure = 200 Torr, background pressure in the beam chamber = 0.3 mTorr and orifice diameter = 0.065 mm) the Mach disk is calculated to occur at about 35 mm downstream of the nozzle. Our measurements are thus conducted well within the cold regions of the beam, since the supersonic beam is probed about 3 mm downstream of the nozzle. We could not confirm this directly by determining the rotational temperature of a PAH in the jet, but we did measure the rotational temperature of NO_2 seeded into an argon jet. The vibrational band obtained at 585 nm is illustrated in Figure 3. Only a few rotational lines are seen in the P and R branches and these show a peak intensity at J=2 or 3. The rotational temperature is determined to be 6 K. There is no reason to believe that PAH's in an argon jet would have higher rotational temperatures. If anything, these should be lower because of the considerably smaller rotational constants of PAH's.

The preparation of samples depends greatly on the type of information being sought. In experiments conducted to obtain spectra only a quantity of solid PAH typically in the range of a mg or less is placed into the sample well of the beam nozzle insert. In experiments to determine a PAH quantitatively a method is used developed by Yamada and Winefordner (3), and it is necessary to limit the sample size to the range of 1 to 140 μg. This is achieved by first placing a precisely measured aliquot of a dilute PAH/acetone solution into the sample well using an Eppendorf micro-pipette and then driving off the solvent by heating and ventilating. The dried sample is inserted into the beam nozzle which is being maintained at the desired temperature. The sample inserted into the stagnation chamber rapidly rises to the desired temperature. The PAH vapour is mixed with an inert gas such as helium or argon and the mixture is expanded into a supersonic jet through a pinhole into a low pressure beam chamber. A dye laser is tuned to a resonant frequency and the resulting fluorescence is measured with a photomultiplier detection system - in our case the system described earlier in this section. The signal rises to some plateau value, ideally remains there briefly and then declines to zero as the sample is depleted. The signal can be displayed on a chart recorder strip chart or digitized and stored in a computer. The integral of the signal with respect to time is proportional to the amount of PAH in the sample. A calibration plot can be determined by varying the sample size. The peak height of the signal depends only on the temperature provided that there is enough material to establish equilibrium between the solid and its vapour even if only momentarily. The duration of the signal peak is determined by both the stagnation temperature and the amount of sample. The integrated signal depends only on the amount of sample.

For this quantitative technique to be valid it is essential that the photomultiplier be operated in its linear response range and that the ground state population of the PAH not be significantly depleted by absorption of laser photons. As mentioned earlier the photomultiplier used to measure the PAH fluorescence has a linear response up to 1 ma of anode current or a 500 mv signal across a 50 ohm resistor. Care was taken to limit signal levels to below this limit by reducing the laser intensity with neutral density filters. Depletion of the ground state population of a PAH may result in a non-linearity between fluorescence signal and laser pulse energy, even when the photomultiplier is well within its linear range of operation. The range of laser pulse energies over which the fluorescence intensity shows linear behaviour varies from one PAH to another and must be set empirically for each PAH. Normally the laser pulse energy incident on the supersonic beam is varied with the aid of neutral density filters. For strong absorbers it may be necessary to use very low pulse energies. For example, it is necessary to maintain laser pulse energies at less than 0.3 μJ when studying perylene.

Analog signal pulses from the photomultiplier are processed with an Evans Associates gated integrator for noise reduction and then displayed with the aid of a strip chart recorder. The area under the resulting curve is obtained manually directly from the trace. Since this area is proportional to the laser pulse energy, the laser pulse energy is monitored and used to normalize the area. Until the present time the absolute energy has been measured immediately prior to and after a sample run and an average pulse energy determined. The two measurements have been found to agree well with each other; however, to take into account any variations in laser energy during the course of a sample run, a separate strip chart record of the laser energy will be generated of the output of the monochromator photomultiplier and used to establish the laser wavelength.

2.2 Shpol'skii Spectroscopy

The experimental setup has been described in detail in the Proceedings of the Fifth (4) and Sixth Technology Transfer Conferences (2), and will only be given in outline here. The sample is dissolved in a normal alkane solvent, typically n-octane, and diluted to 100 ng/mL or less. An aliquot is removed with an Eppendorf micro-pipette and transferred to a cell made of copper fixed with a quartz window. This cell is inserted into a well in a copper block attached to the cold-head of a CTI-Cryogenics Model 21 refrigerator after first freezing the solution by dunking in liquid nitrogen. Spectroscopic measurements are carried out when the sample temperature reaches a value between 10 and 20 K. Both excitation and fluorescence spectra are obtained. The latter are generated with either a nitrogen laser or a dye laser tuned to a fixed wavelength that is strongly absorbed. The fluorescence from the sample is collected by a lens and focussed through a series of filters onto the slit of a 0.3 m McPherson Model 218 scanning monochromator to which is attached a EMI 6256 photomultiplier mounted in a EMI FACT-50MKIII refrigerated housing. This photomultiplier has been wired for linear signal response up to 0.7 ma anode currents. The same precautions with respect to photomultiplier saturation and ground population depletion must be exercised in these experiments as were discussed in the previous section.

In the linear range of signal dependence on laser pulse energy the amplitude of the fluorescence signal pulse coming from the photomultiplier must be dependent linearily on the concentration of PAH in the frozen matrix. This allows one to determine PAH's quantitatively. Initially one must set up a series of calibration curves for each PAH, typically in the form of signal peak intensity plotted against laser pulse energy. However, to avoid uncertainties arising from unexpected variations in laser pulse energy or other experimental factors it is advisable to incorporate an internal standard into each sample analysed. We have selected perylene, because it is a relatively strong absorber and because its fluorescence occurs far enough from that of other PAH's in our list not to cause problems arising from spectroscopic interferences. Thus, in a typical analysis a measured amount of perylene is added to the sample to be analysed. Fluorescence is excited either by the nitrogen laser or by the nitrogen pumped dye laser tuned to a wavelength at which absorption is strong, but well to the short wavelength side of the fluorescence to be observed in order to minimize interference from scattered laser radiation. The fluorescence is dispersed by the McPherson monochromator and peaks belonging to the perylene and other PAH's in the sample are identified. Peak heights are measured and used in the quantitative determination. Because the original sample might itself contain perylene, a fluorescence spectrum of the sample is first obtained without added perylene and a second one is obtained with the added perylene. In this way we can subtract the signal associated with the perylene originally in the sample and use the residual signal as a calibration marker.

The analog signal pulse from the McPherson monochromator is processed by an Evans Associates gated integrator for signal/noise improvement and displayed on a strip chart. Peak heights are measured and taken to be relative measurements of the concentration of PAH in the sample.

3.0 Results and Discussion

3.1 Jet-Cooled Spectroscopy

Figure 3 shows a vibrational band of NO_2 associated with the absorption of laser radiation at 585.1 nm. The top trace is a laser excitation spectrum of NO_2 seeded in a supersonic jet of argon; the lower of NO_2 gas at room temperature. The jet spectrum indicates a rotational temperature of about 6 K. These spectra illustrate quite dramatically the simplification that results from cooling even tri-atomic gases. Figure 6 shows Shpol'skii and jet-cooled excitation spectra of 9-methylanthracene. The two features in the top trace obtained in the beam are the same vibrational bands as the two leftmost features in the bottom trace obtained in a frozen matrix. The jet-cooled spectrum is shifted about 1.6 nm towards shorter wavelengths with regard to the Shpol'skii spectrum. This shift arises because in the jet the PAH molecules are essentially isolated whereas in the matrix they are subject to interaction with solvent molecules.

Jet-cooled spectra of benzo(a)pyrene [B(a)P], benzo(ghi)perylene [B(ghi)P], pyrene [Py] and perylene [P] are shown in Figures 7 to 10. Each feature is actually a vibrational band with unresolved rotational structure. The half-widths of the bands shown arise mainly from the low resolution of the laser beam, which is about 0.06 nm. Fourmann et al (4) have measured the rotational band-width of perylene to be 1.8 cm^{-1} in a jet with a rotational temperature of 4 K. This corresponds to about 0.03 nm. at the excitation wavelengths used in our study.

Figure 11 consists of two plots of signal vs time obtained in a quantitative experiment on Py - one for 140 ug and the other for 1.4 μg of Py. These experiments were conducted with the gated integrator set for a signal/noise improvement ratio of about 25. We estimate that the detection limit for Py of our system as it presently stands is approximately 1 μg. A pulsed supersonic beam with an open time of, say, 0.5 ms, an orifice of 0.5 mm diameter and operated at a repetition rate of 10 Hz would reduce the detection limit by increasing the beam density and the total time required to expel the entire sample. Such a beam would only be on for 5 ms out of each second of real time.

Figure 12 plots the signal integrated over time against the mass of the sample for Py and B(a)P. Both plots were obtained under conditions where the signal was not affected by saturation effects. The high degree of linearity of the plots is evident and underlines their validity as quantitative calibration plots. We are presently determining such calibrations for P and B(ghi)P. While we have not yet attempted to analyse a mixture of PAH's let alone an environmental sample, we are confident that given our capabilities with regard to resolution, which is related to selectivity, and sensitivity we shall successfully achieve this goal. Mr. John Lai is the graduate student responsible for the beam work reported here.

3.2 Shpol'skii Spectroscopy

Our attempts to quantify this technique have been hindered by problems with the nitrogen laser dedicated to this project. Some preliminary attempts to obtain a calibration plot for B(a)P with P as an internal reference standard have demonstrated a linear dependence of signal amplitude on the concentration, but these do not represent the best that we can do. At this moment we believe that the problems with the nitrogen laser have been satisfactorily resolved and look forward to a successful resumption of our experiments.

Despite problems with the nitrogen laser progress has been made. We have now defined the limits of signal saturation and have re-measured some of the spectra under linear conditions that were reported at the previous Technology Transfer Conference. In addition we have established upper bounds to the detection limits for B(a)P and P. These are concentrations of 1 ng/mL in each case established by observing fluorescence excited by a nitrogen laser. Given that our aliquots have typically been 600 μL delivered to a cell of 700 μL volume, this concentration limit corresponds to a mass limit of 0.6 pg. This is not the true mass limit, because only a small fraction of the sample is actually probed by the laser. Steps are underway to reduce the volume of the sample cell to less than to 0.1 of its present value, which would then reduce our detection limit to less than a picogram. We expect to improve on this considerably by using a tunable dye laser as the excitation source, which will permit us to excite at more favourable wavelengths than the 337 nm wavelength of the nitrogen laser. This work is being conducted by Mr. Harold Malle, who is a graduate student working towards his M.Sc.

3.3 A Comparison of the Two Techniques

The most obvious contrast between jet-cooled and Shpol'skii spectroscopies lies in their sensitivities. Shpol'skii spectroscopy is by far the more sensitive of the two in quantitative determinations of PAH. This advantage may be offset by other considerations. These sensitivities were determined for pure samples of PAH. However, of greater interest are PAH's in environmental samples. The only environmental samples we have analysed so far by Shpol'skii spectroscopy were fractions from HPLC analysis, whereas we would really desire to start with the actual environmental sample itself; e.g. with the trapped material on a Hi-Vol filter. This immediately poses the problem of extraction, with possible loss of material. On the other hand, when using jet-cooled spectroscopy, we would, in principle, be able to place a section of the Hi-Vol filter directly into the heated section of the beam nozzle and in this way eliminate any extraction steps. Such a direct analysis would be able to quickly identify and quantify selected PAH's in an environmental sample and thereby play an important part in environmental analysis. For example, it could provide a quick guide to the PAH content of an environmental sample. In addition, it could serve as an indicated of how efficient various extraction and cleanup steps are that are required as preparatory to HPLC analysis, for example, which is a common analytical tool.

In jet-cooled spectroscopy one uses up a sample during each analysis. This means that a separate sample must be analysed for each PAH chosen. The Shpol'skii technique allows one to analyse for several different PAH's using the same sample and in this way it is less cumbersome than the jet-cooled technique, when it is desired to monitor several compounds simultaneously. The two techniques are comparable when it is desired to monitor a single PAH in a number of samples.

Shpol'skii quasi-lines are less than 0.1 nm in width for matrix temperatures of 20 K or less, whereas vibrational bands in jet-cooled spectra are in the range of 0.03 nm in width. These widths determine selectivity and it is seen that the two techniques are comparable in this regard.

4.0 References

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3. S. Yamada and J.D. Winefordner, Spectroscopy Letters, 18(2), 139-151, 1985.

4. F.J. Morgan, G. Parnell, S.V. Filseth and C.M. Sadowski, Proc. Tech. Trans. Conf. No. 5, 871-894, 1985.
5. B. Fourmann, C. Jouvet, A. Tramer, J.M. LeBars and Ph. Millie, Chem. Phys. 92, 25-42, 1985.

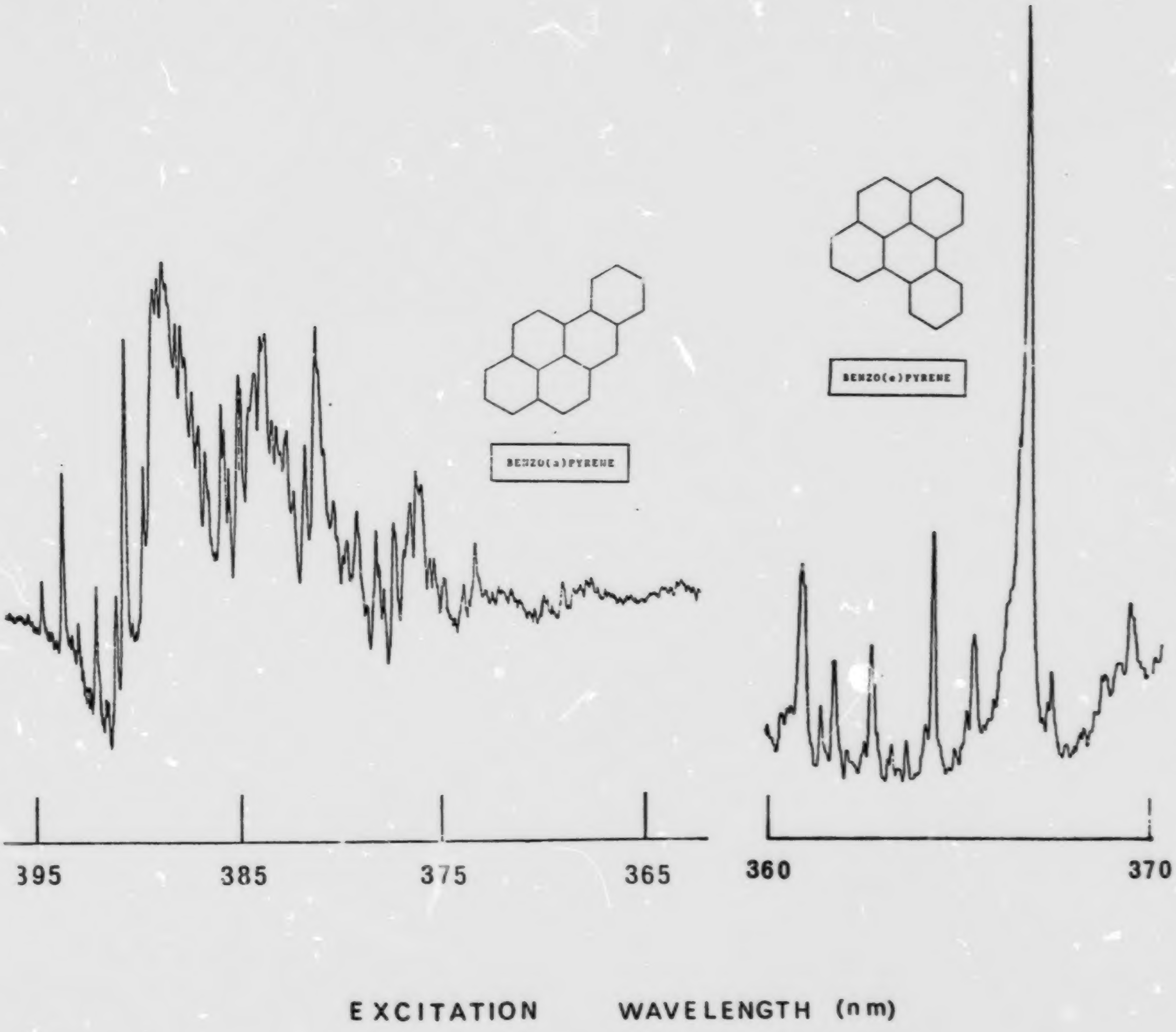

FIGURE 1: Shpol'skii Laser Excitation Spectra of Benzo(a)Pyrene and Benzo(e)Pyrene

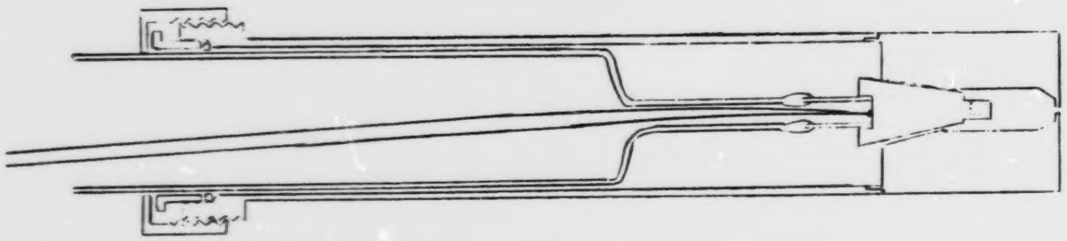

FIGURE 2: Schematic of the Supersonic Beam Nozzle

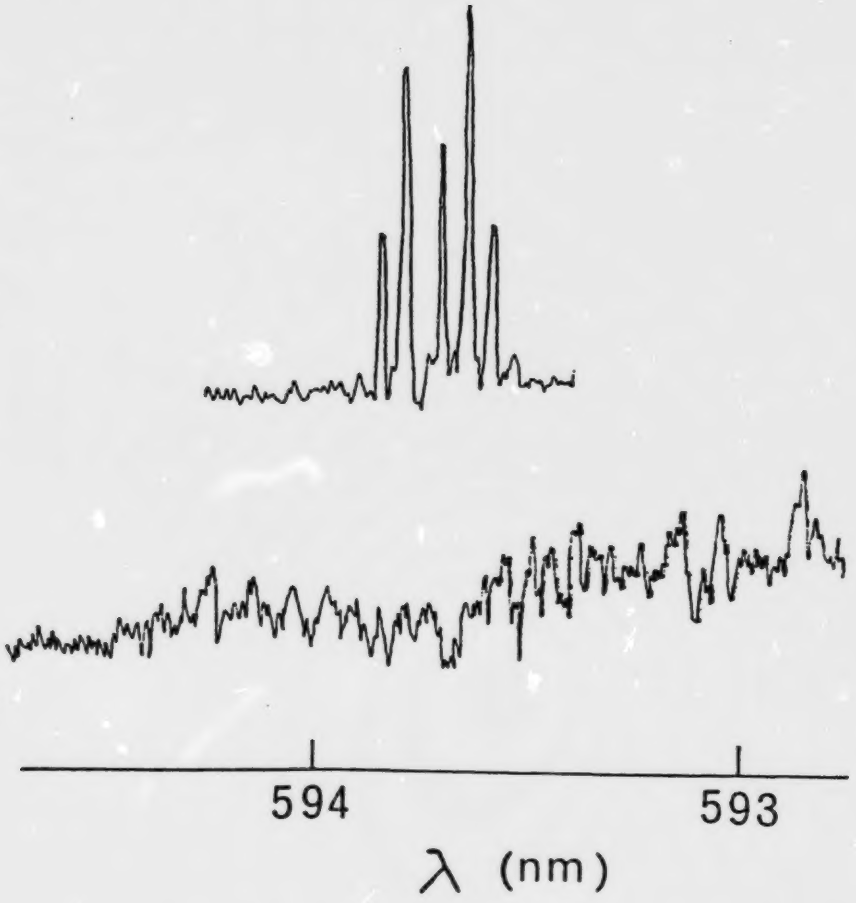

FIGURE 3: Laser Excitation Spectra of NO_2
a) Lower Trace - Room Temperature, T = 292K
b) Upper Trace - Jet-Cooled, T_{ROT} = 6K

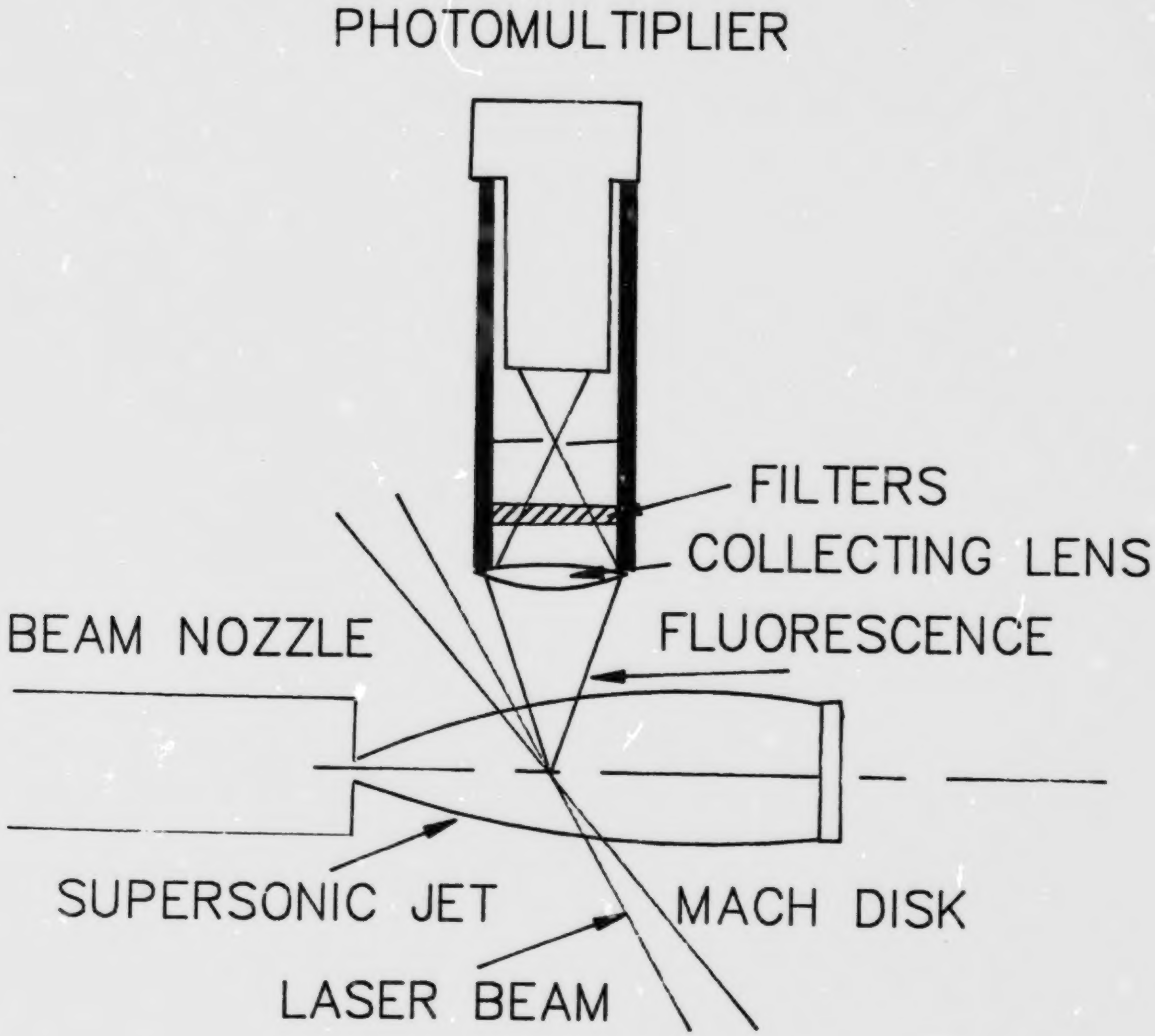
PHOTOMULTIPLIER
FILTERS
COLLECTING LENS
BEAM NOZZLE
FLUORESCENCE
SUPERSONIC JET
MACH DISK
LASER BEAM

FIGURE 4: The Supersonic Beam Apparatus

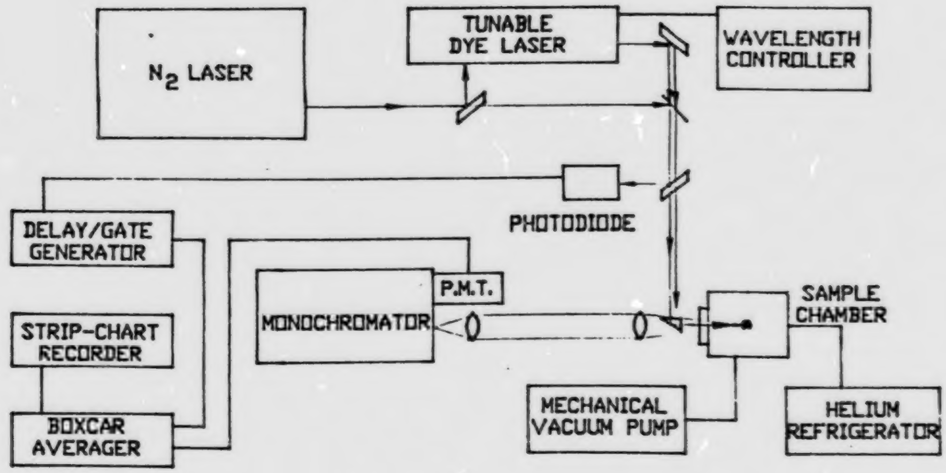
N₂ LASER
TUNABLE DYE LASER
WAVELENGTH CONTROLLER
PHOTODIODE
DELAY/GATE GENERATOR
STRIP-CHART RECORDER
BOXCAR AVERAGER
MONOCHROMATOR
P.M.T.
SAMPLE CHAMBER
MECHANICAL VACUUM PUMP
HELIUM REFRIGERATOR

FIGURE 5: Shpol'skii Apparatus

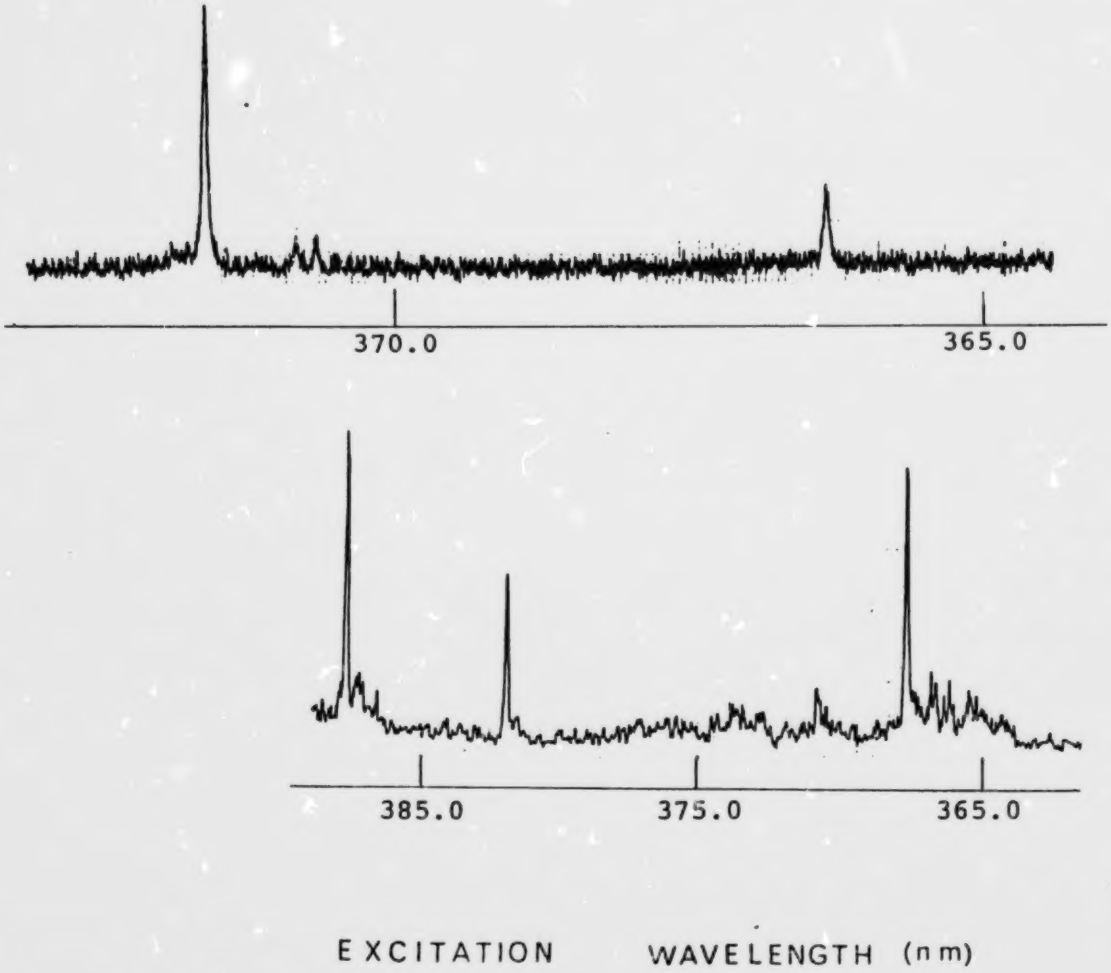

FIGURE 6: Laser Excitation Spectra of 9-Methylanthracene
a) Lower Trace Matrix Cooled
b) Upper Trace Jet-Cooled

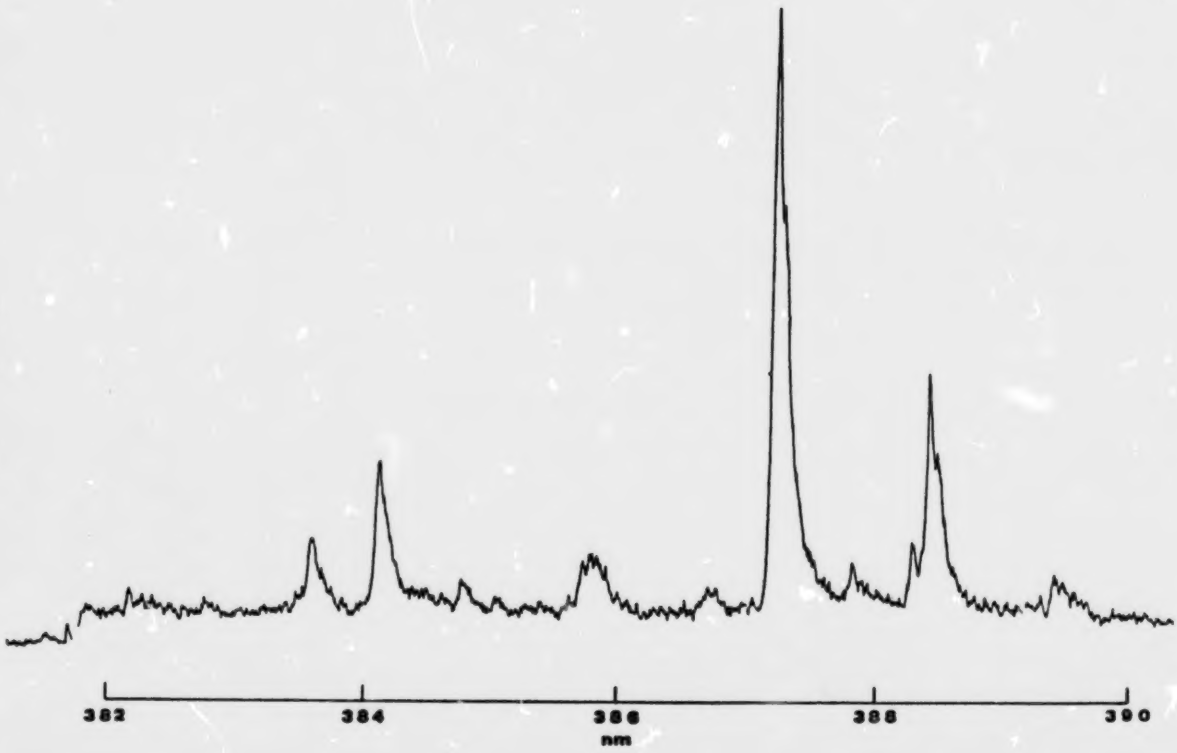

FIGURE 7: Jet-Cooled Laser Excitation Spectrum of Benzo(a)Pyrene

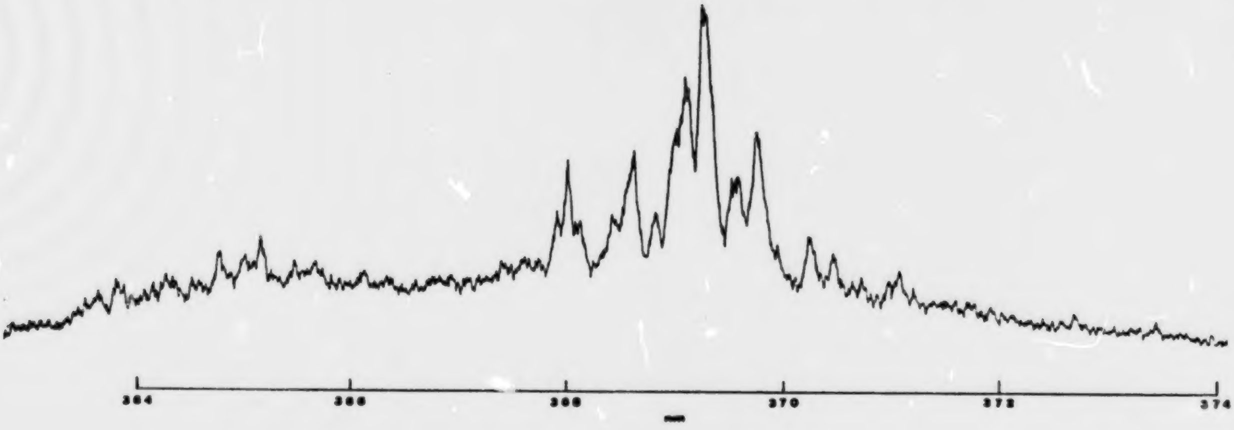

FIGURE 8: Jet-Cooled Laser Excitation Spectrum of Benzo(ghi)Pyrene

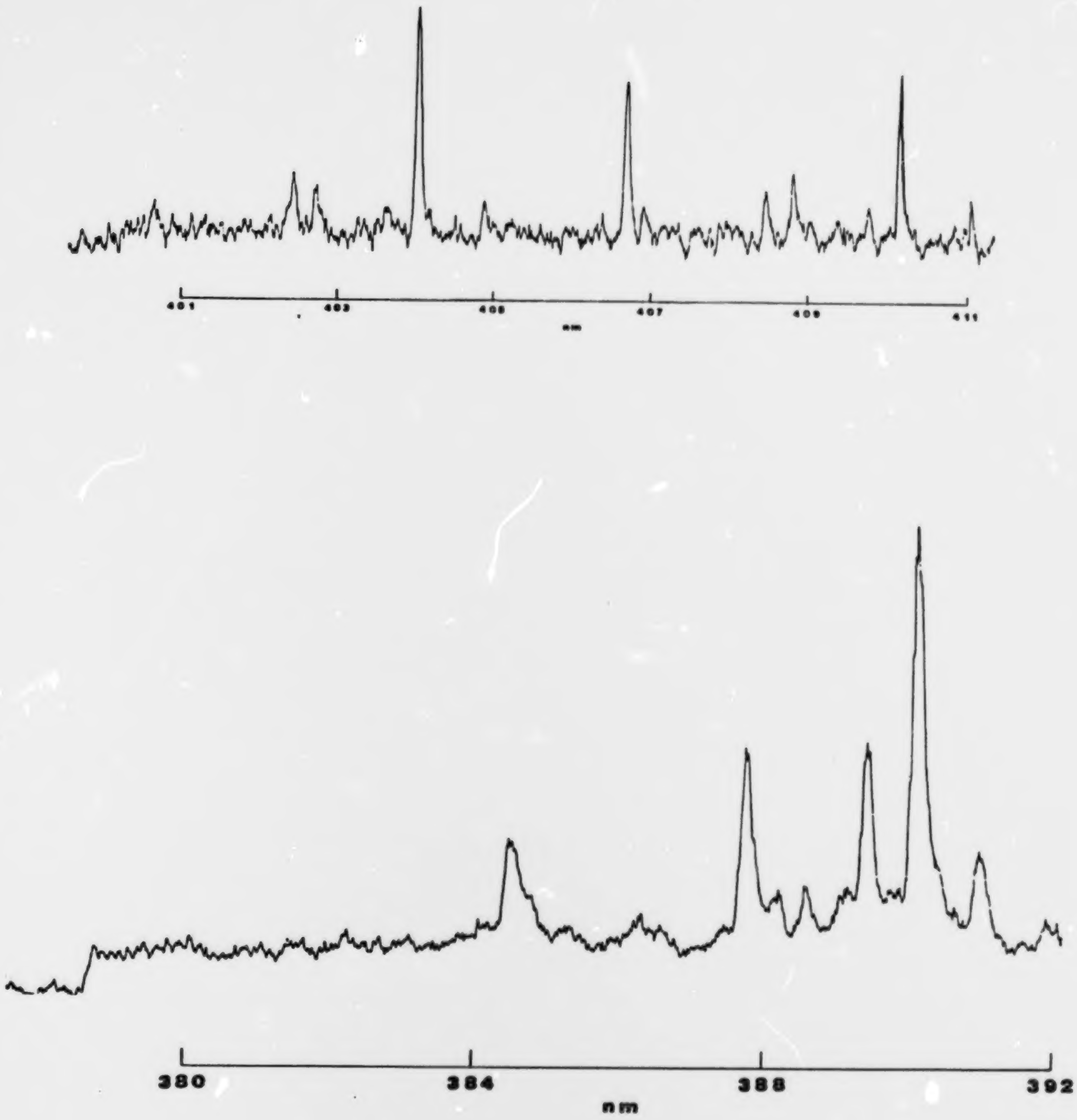

FIGURE 9: Jet-Cooled Laser Excitation Spectrum of Pyrene

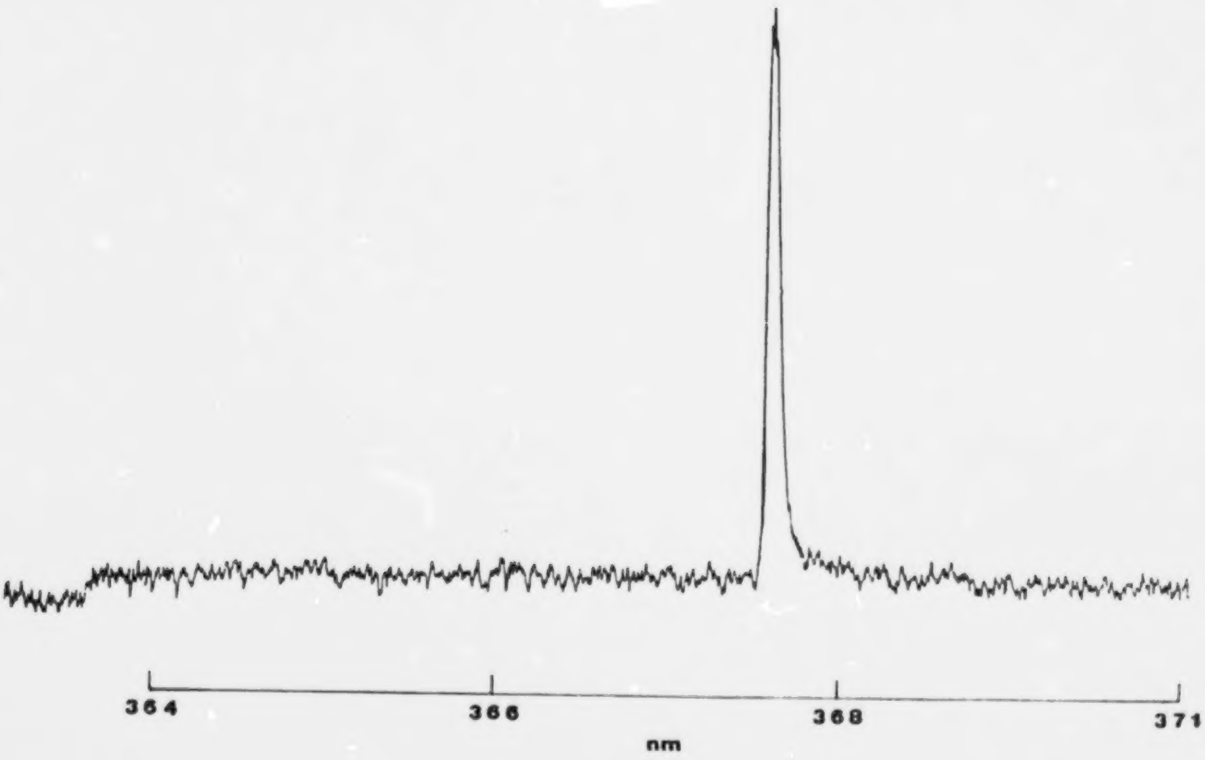

FIGURE 10: Jet-Cooled Laser Excitation Spectrum of Perylene

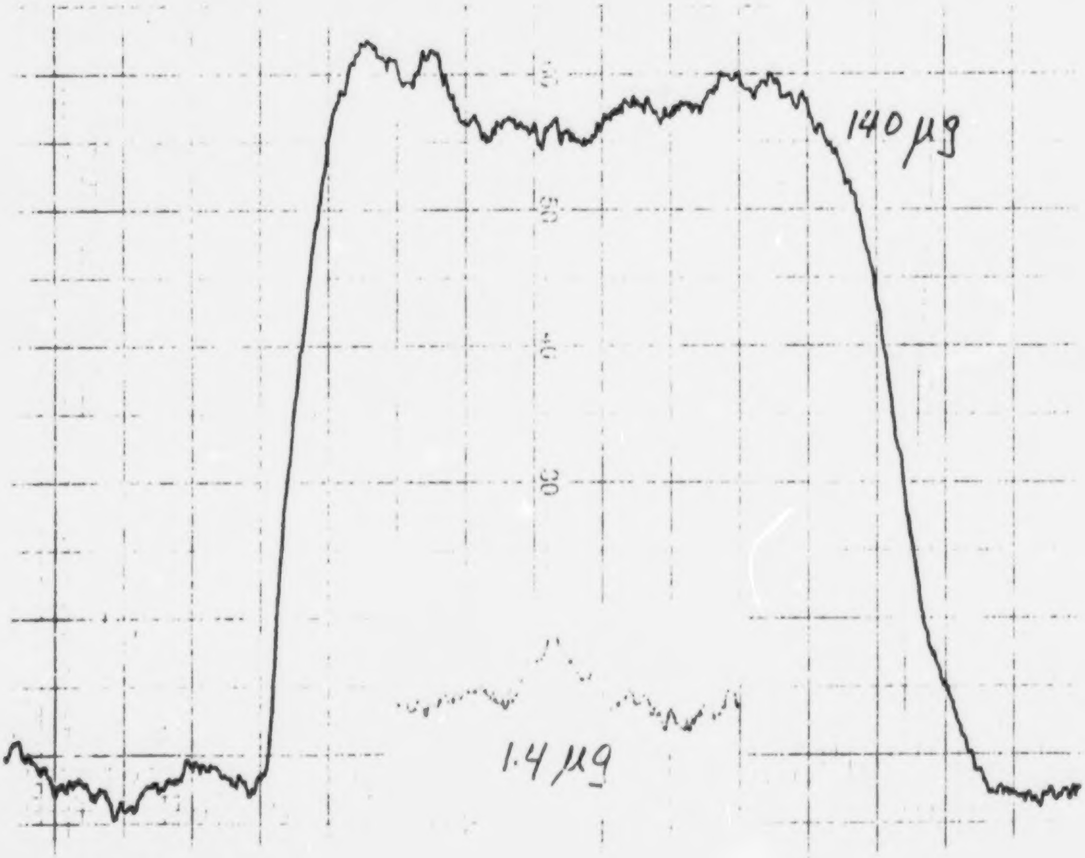

FIGURE 11: Laser Excited Fluorescence Signal vs Time for Pyrene in a Supersonic Jet of Argon

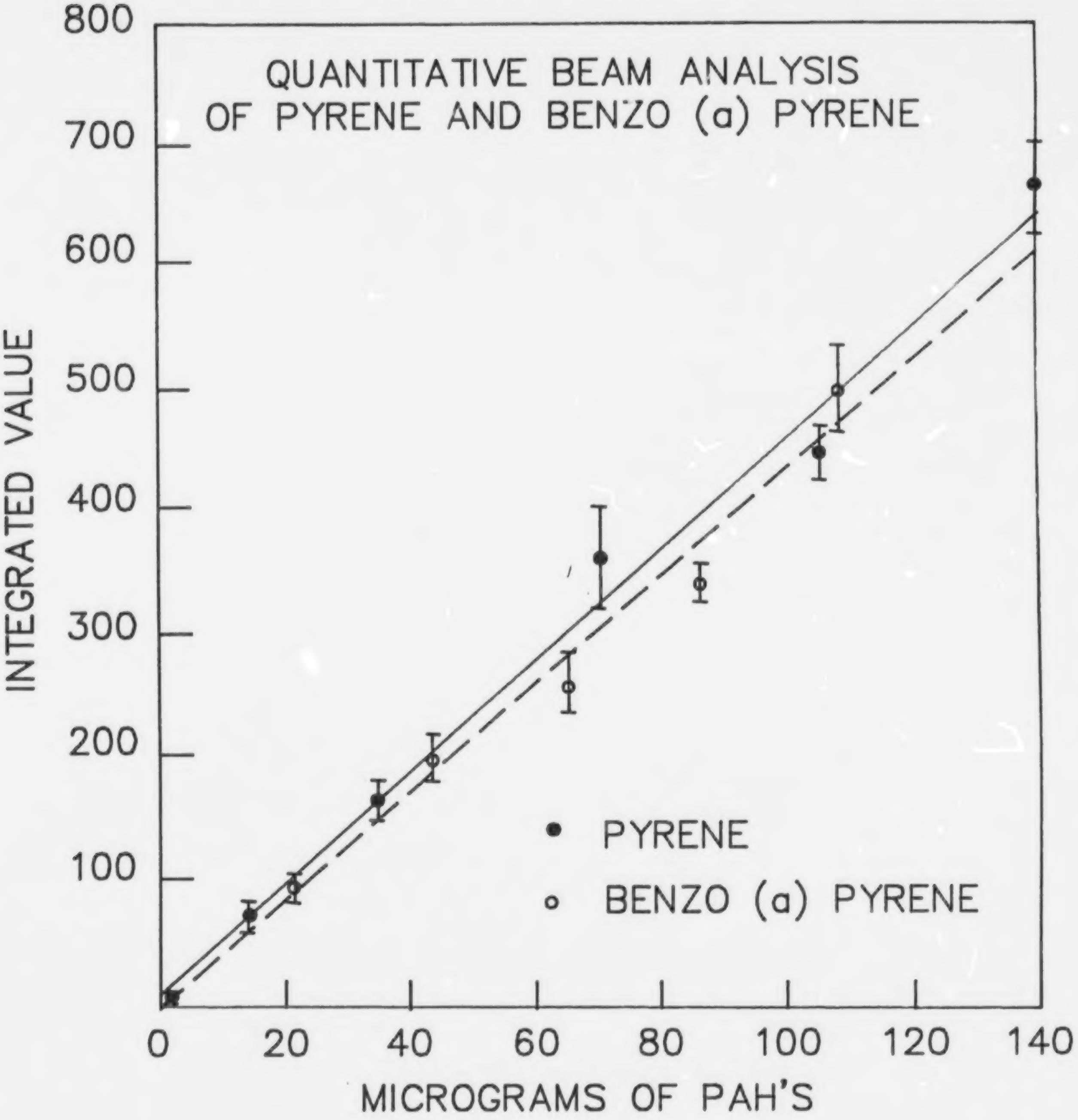

FIGURE 12: Plots of Time-Integrated Fluorescence Signals vs Mass of Sample from Quantitative Beam Analysis

NEW GENERAL SYNTHETIC METHODOLOGY FOR EXPEDIENT PROVISION OF ISOMERICALLY PURE PAH ANALYTICAL STANDARDS

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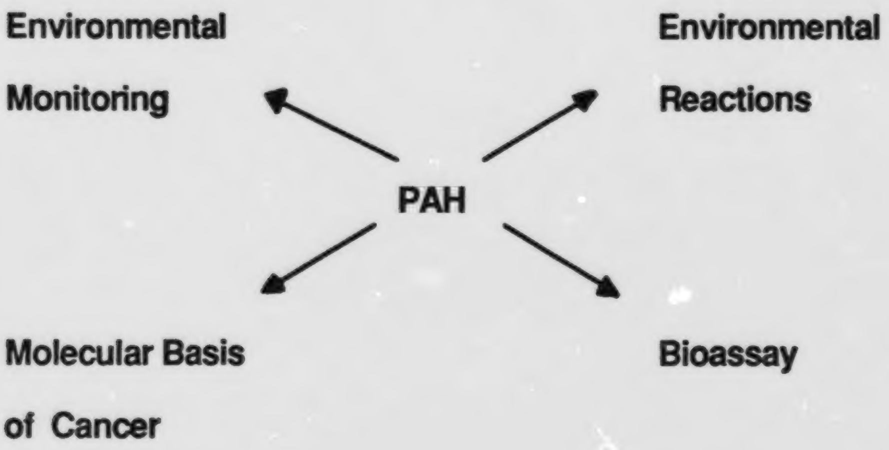
INTRODUCTION

Polycycilic aromatic hydrocarbons constitute a major class of organicpollutants widely dispersed in the environment arising from the incomplete combustion of fossil fuels and other organic matter (1). Human exposure to PAH through tobacco smoke and in certain occupations and urban environments has led to the strong inference that these compounds are important cancer causative agents in man (2) and thus has led to extensive research into the formation, occurrence, detection, chemistry, and metabolism of PAH (3). Interest in the corresponding aza-PAH is of more recent origin, having been stimulated by their discovery in samples of particulate matter, street dust, automotive exhausts, lake sediments, and cigarette smoke (1b, 4). In view of evidence of theircarcinogenic nature, aza-PAH have prompted systematic characterization and biological testing as well (5). Methyl-PAH are always components of environmental PAH samples and recent studies have demonstrated that methyl substitution confers a remarkable enhancement in the tumerogenicity of PAH. Finally, the discovery of potent direct acting mutagenicity of nitro-PAH in 1980 and the accumulating evidence of their wide distribution resulting from diesel exhaust, fly ash, photocopier fluids, and cigarette smoke has resulted in increased research in the detection and elucidation of biological activity of this class of compounds (8).

Recent studies have demonstrated that the carcinogenic activity of PAH is expressed via prior metabolic activation (2b, 9). The primary metabolite arene oxides (proximate carcinogens), formed by enzymatic addition of an atom of oxygen, are relatively unstable and are further modified to dihydrodiol epoxides (ultimate carcinogens) which covalently modify DNA (10). The Bay Region theory of carcinogenesis suggests that dihydrodiol epoxides of bay regions of PAH are important for the initiation of cancer (9, 10, 11), although it cannot explain the effects of methyl substitution on carcinogenic activity (12).

Organic synthesis is the **sine qua non** condition of all PAH research. PAH compounds are required in high analytical purity for studies concerning a) environmental monitoring of their fate and distribution, b) monitoring of their environmental reactions (e.g. with ozone, NO_x), c) comprehensive understanding of their metabolic conversion to the ultimate carcinogens and therefore insight into the molecular basis of cancer and d) bioassay of newly discovered PAH to establish mutagenicity/carcinogenicity levels to warn of potential danger **(Figure 1)** .

Figure 1



Recent work in our laboratories has led to the development of a new general methodology for the synthesis of a variety oF PAH and aza-PAH of environmental interest based on the aromatic directed metalation strategy **(Figure 2)** (13). Extension of this tactic has also allowed the preparation of previously inaccessible halo- and methyl-PAH involving regiospecific silicon protection of aromatic C-H and C-methyl sites **(Figures 3,4, 5, and 6)**. Herein we review our work and new results connecting the directed metalation strategy with other modern synthetic methodologies: a) silicon activation for the preparation of nitro-PAH **(Figure 7)**, b) silicon activation for regiospecific synthesis of indanols **(Figure 9)**, and c) transition metal catalyzed cross coupling reactions leading to nitro-biphenyls **(Figure 10)**. These reactions constitute prototypes of new methodologies promising to provide PAH and nitro-PAH by economic, efficient, and regioselective routes which avoid problems of isomer separation and excessive handling of carcinogenic substances as are normally associated with the available classical methods.

IMPROVED PREPARATION OF PAH-QUINONES AND CORRESPONDING PAH

As a direct consequence of general approaches towards the preparation of anthraquinones **2** and acridones **3** using ortho lithiated benzamides **1 (Figure 2)**, a number of PAH-quinones and PAH-heterocyclic quinones were prepared (14). A general, one-pot procedure was developed involving metalation (sec-BuLi), treatment with aromatic aldehydes, metalation, and aerial oxidative workup. Subsequent mechanistic investigation (15) led to the suggestion that excess base would have a favorable effect on the yields of this reaction and a new procedure was developed involving metalation with four equivalents of sec-BuLi followed by Jones oxidation. Using this procedure, a number of PAH-quinones were obtained in significantly improved yields compared to those achieved previously (15) **(Table 1).** Although the scope of this method has not been exhaustively evaluated, its limitations will most likely arise in reactions of heterocyclic systems (e.g. pyridine) which are highly susceptible nucleophilic attack by reagents. Further mechanistic investigations currently in progress (16) may shed more light on the potential of this short synthesis of PAH-quinones.

Since PAH-quinone to corresponding PAH conversion is a standard, well-documented reaction (17), the overall route represents an efficient regimen which competes favorably with reported classical syntheses of certain PAH compounds (18). To demonstrate this, we have converted several of the PAH-quinones to the PAH (e.g. benz[a]anthracene, dibenz[a,c]anthracene, and dibenz[a,h]anthracene) using the aluminum tricyclohexoxide in cyclohexanol method (19).

REGIOSPECIFIC ROUTES TO PERI-METHYL-PAH AND AZA-PAH USING SILICON PROTECTION PROTOCOL

Although Newman has carried out extensive systematic work concerning the synthesis of monomethylbenz[a]anthracenes (20), many methyl-PAH are poorly accessible owing to the complexity of existing synthetic methods. Recent work in our laboratories has demonstrated that the trimethylsilyl group functions effectively to mask a) the more reactive metalation site ortho to a carboxamide and b) the ortho methyl moiety in an ortho-toluamide, thus allowing metalation and electrophile introduction into the alternate ortho positions (21). Since silicon groups can be easily introduced (RLi/TMSCl) and removed (CsF or tetra n-butyl ammonium fluoride (TBAF)), this method allows rapid entry into new diversely functionalized aromatic systems (21).

Following work concerned with the development of methodology and its application to the synthesis of naturally occurring anthraquinones (22), we focussed on its utility for the synthesis of peri-methyl PAH **(Figure 3)** (23). Thus treatment of the bis-trimethylsilyl o-toluamide (4) under standard metalation conditions followed by sequential reaction with 2-naphthaldehyde, CsF, and p-toluenesulfonic acid (TsOH) afforded, without purification of intermediates, the phthalide **5** in 52% overall yield. Taking advantage of techniques previously developed in our laboratories (22), the intermediate **5** was hydrogenolized, cyclized and oxidized to give 11-methyl-7,12-benz[a]anthraquinone **6** in 31% overall yield based on **4**. Since the conversion of **6** into 7,11,2-trimethyl-benz[a]-anthracene has been previously achieved, this constitutes a rapid and efficient route to this highly carcinogenic substance. Using identical sequences of reactions, the preparation of the 8-methyl-7,12-benz[a]anthraquinone and 10-methyl-9,14-dibenz[a,c]anthraquinone from 2-naphthaldehyde and 9-phenanthrene carboxaldehyde respectively was achieved in good overall yields (23). These quinones are also immediate precursors to the corresponding methyl-PAH by known reductive methods (19).

We envisage that the combination of our new method of ortho N-arylamination (24) coupled with the silicon protection tactic would provide new routes to methyl substituted acridones and hence the corresponding aza-PAH. As an exploratory experiment investigated recently, the lithiated species **7 (Figure 4)** was treated with the anilido-cyano cuprate **8.** Following oxygenation and the standard desilylation, the o-methyl N-arylanthranilamide **9** was obtained in 48% yield. Direct Friedel-Crafts cyclization using heptafluorobutyric acid (HFBA) afforded 1-methyl acridone **10** in good overall yield. Since the reduction of acridones into the corresponding acridines is a well established procedure (25), the overall route constitutes a general route to a number of environmentally significant aza-PAH.

HALO-PAH USING SILYLATED BENZAMIDE INTERMEDIATES

In view of the widespread occurrence of chloroaromatic pollutants (PCBs, dioxins, chlorobenzene) and their continued incineration (26), interest in the detection and analysis of chloro-PAH and halo-PAH in general has increased significantly in recent years(27). Chloro-PAH have been investigated to determine the effect of chloro substitution on the metabolism of PAH (28) while bromo-PAH have been detected in gasoline and diesel fueled vehicle emissions. Structure-carcinogenic activity correlation studies on bromo-PAH and fluoro-PAH have been reported (30) and the latter class has been used for 'markers' to establish the site of metabolic activation (31).

As an extension of the use of silicon protection protocol in the context of the directed ortho metalation reaction described above, we developed regiospecific routes to several bromo-, chloro-, and fluoro-PAH quinones (32, 33). The readily available 2,6-dibromobenzamide **11 (Figure 5)** was subjected to monometal-halogen exchange followed by treatment with either 1-napthaldehyde or 2-naphthaldehyde, and the crude products derived were cyclized with TsOH in refluxing toluene to afford the phthalides **12** and **13** in 67% an 78% overall yields respectively. Slight modification (32) of the regimen described above for the preparation of methyl-PAH **(Figure 3)** led, in several steps, to the bromo benz[a]anthraquinones **14** and **15** which, as in the pevious anthraquinone examples, could be converted into the bromo-PAH and dimethylbromo-PAH using standard methodology developed by Newman (30).

Similarly, the highly condensed bromo-PAH quinones **16** and **17** were prepared by quenching the monolithio species derived from **11** with either 9-phenanthrene carboxaldehyde or 1-pyrene carboxaldehyde respectively and following the standard phthalide to anthraquinone procedure described above for methyl-PAH.

The knowledge that meta-related chloro or fluoro and carboxamide substituents undergo regiospecific ortho metalation in the site common to both (34) allowed the synthesis of the corresponding chloro- and fluoro-anthraquinones using the silicon protection concept **(Figure 6)** (33). Thus standard metalation and silylation of **18,** X = C, F, smoothly led to the formation of the respective silylated products **19** which upon further metalation and condensation with benzaldehyde, and TsOH cyclization furnished the chloro- and fluoro-phthalides whose conversion into the corresponding anthraquinones 21 **followed the procedures established for the preparation of the bromo-PAH quinones described** above. These examples demonstrated the utility of metalation-silylation strategies for convenient access to certain halo-PAH in high yields and short order. The potential for synthesis of more highly condensed halo-PAH appears to be promising.

SILYLATED PAH QUINONES AS INTERMEDIATES FOR NITRO-PAH

Cognizance of the facile ipso nitrodesilylation of aryl silanes (35, 36) suggested that silylated anthraquinones **24** may serve as potential intermediates for the corresponding nitro-PAH systems **(Figure 7).** To achieve this end, the ortho silylated benzamide **22** was metalated, treated with 2-naphthaldehyde, and cyclized with TsOH to give the silylated phthalide **23** in good overall yield. The conversion of **23** into the corresponding anthraquinone **24** and thence into the nitro-PAH, **25,** currently in progress, may necessitate the prior reduction of the quinone moiety in order to activate the ipso nitrodesilylation process (35, 36). The concommitant reduction of the nitro group, if it occurs, will be redressed by a reoxidation reaction (37).

A GENERAL 1-INDANOL SYNTHESIS VIA FLUORIDE-INDUCED INTRAMOLECULAR CARBODESILYLATION. POTENTIAL APPLICATION TO FLUORENES

Although the classical Friedel-Crafts reaction is a well-travelled route for annelation of 5-, 6-, and 7-membered ring ketones to aromatic substrates (38), its regiospecificity is dictated by the normal electrophilic substitution rules which preclude the preparation of certain substituted systems without resorting to protection divergencies and multi-step regimens. A case in point is the intramolecular Friedel-Crafts reaction of methoxy-substituted **26 (Figure 8)** which invariably leads to para- (27) and not the desired ortho-substituted product. As a result of our interest in connecting arylsilane derived methodology to the directed metalation reaction and the recent demonstration by Effenberger of fluoride-induced ipso carbodesilylation in reactions of arylsilanes with aromatic aldehydes (39), we sought to devise new routes to 7-methoxy-1-indanols **34 (Figure 9)**, synthons which are of demonstrated utility a number of applications and of potential use for the preparation of nitrofluorene PAH.

To derive the key intermediates **(Figure 9)**, the silylated meta-anisamide **29** was sequentially treated with diborane and vinyl chloroformate (40) to afford the unstable benzyl chloride **30** which, according to the excellent procedure of Kozlewski (41), was smoothly converted into the benzaldehyde **31**. Wadsworth-Emmons-Horner reaction followed by hydrogenation gave the phenyl propionate **32**, $R^1 = H$, $R^2 = Me$, whose conversion into the corresponding aldehyde **33** was achieved by standard diisobutylaluminum hydride (dibal) reduction. The methyl substituted aldehyde **33**, $R^1 = Me$, $R^2 = H$, was similarly obtained while the corresponding dimethyl derivative **33**, $R^1 = R^2 = Me$, was prepared by a different route (42).

When the three aldehydes **33** were subjected to reaction with CsF in anhydrous DMF, the 1-indanols **34** were obtained in 50-70% yields. Since the highest yields are obtained on **33**, $R^1 = R^2 = H$, the most likely system to undergo fluoride-catalyzed aldolization (43), the yield appears not to be reflective of such a process.

To test the possibility of an intramolecular electrophile-induced ipso desilylation, a well-established method without sufficient synthetic application (36), the acid chloride corresponding to the ester **32**, R = H, readily obtained by standard base hydrolysis followed by oxalyl chloride treatment, was subjected to reaction with various Lewis acids ($AlCl_3$, $TiCl_3$, $SnCl_4$). In all cases, 5-methoxy-1-indanone, the product of desilylation and normal Friedel-Crafts acylation, was obtained. This result, presumably due to steric factors in the formation of the Lewis-acid coordinated ipso intermediate, mitigates the potential use of the acylium ion induced carbodesilylation process.

In summary, the fluoride-induced intramolecular carbo-desilylation reaction, **33→34** is a useful procedure for the efficient access to 7-methoxy-1-indanols. The application of this method for the construction of fluorene-PAH is currently under investigation in our laboratories.

A NEW NITRO-H PROTOTYPE CONSTRUCTION BASED ON Pd-CATALYZED CROSS COUPLING OF BORONIC ACIDS WITH ARYL BROMIDES

The increasing evidence that nitro-PAH is a widely distributed, highly mutagenic class of environmental pollutants (7) has stimulated analytical and biological research in this area (8). In support of these studies, synthesis and complete characterization of nitro-PAH is a prime requirement. The currently available methods are invariably based on electrophilic substitution and other classical reactions which suffer from low yields, lack of isomeric specificity, and limited scope (8).

We have recently developed a new general method for the construction of unsymmetrical biaryls and heterobiaryls with diverse functionality using a transition metal catalyzed cross coupling reaction of aryl boronic acids with aryl bromides (44). We are in the process of expanding this method to include the preparation of nitro-PAH including nitro-fluorenes(nitro-F), nitro-fluoranthenes(nitro-FA),and nitro-phenanthrenes (nitro-P) (45). The preliminary methodological results are encouraging and these, together with appliction for the preparation of nitro-F are described here.

Following the development of our general protocol **(Figure 10)** (44), we have carried out the cross coupling reaction between the ortho boronic acid benzamide **36,** prepared from the parent benzamides **35** and aryl bromides (ArBr) containing nitro functionality (ortho, meta, para-nitro bromobenzenes have been used). In all cases, high yields of the respective coupling products **37** (Ar = nitro-aromatic) have been obtained.

These successful results provide the impetus to undertake the preparation of nitro-F PAH substances **(Figure 11).** The isomeric NO_2-ortho-bromobenzaldehydes **38,** all of which are available by classical syntheses, will be coupled with phenylboronic acid **39** to give the NO_2-biphenyl aldehydes **40.** The conversion of **40** into the NO_2-F **43** will be carried out in two sequences: either borohydride reduction followed by precedented (46) acid-catalyzed cyclization or oxidation to the carboxylic acid **41** followed by the more classical Friedel-Crafts reaction to the intermediate fluorenone and reduction to the nitro-F (42). Using this prototype sequence of reactions, the synthesis of a variety of nitro-F derivatives (Table 2) and in, projection, the corresponding nitro-fluoranthenes will be feasible.

CONCLUSIONS

The synthesis of a number of PAH, aza-PAH, methyl-PAH, halo-PAH have been achieved by routes which are short, efficient, and avoid excessive contact with intermediates and carcinogenic products. In addition, key synthons have been constructed which will allow the preparation of new methyl aza-PAH, methyl halo-PAH, and several classes of nitro-PAH including nitro-fluorenes, nitro-fluoranthenes, nitro-phenanthrenes, and nitro-benz[a] anthracenes. A sizeable repository of PAH samples are currently available in high purity and new PAH are being synthesized on a continuing basis which will provide the necessary analytical standards for present or future, possibly unanticipated, environmental problems.

ACKNOWLEDGEMENT

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Figure 2

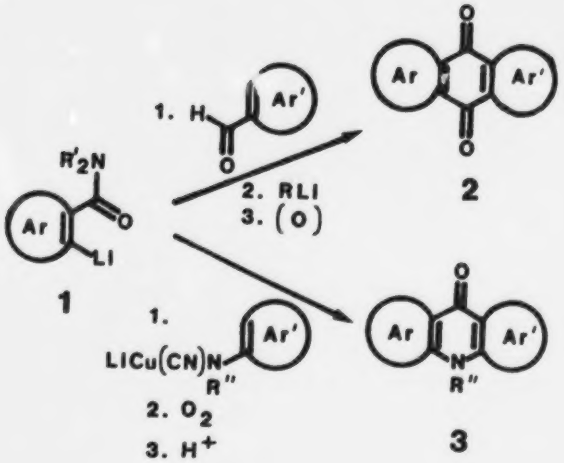


Table 1. PAHs, PAH-Quinones and Aza-PAHs Synthesized in Our Laboratories

PAHs (and Precursor Quinones)

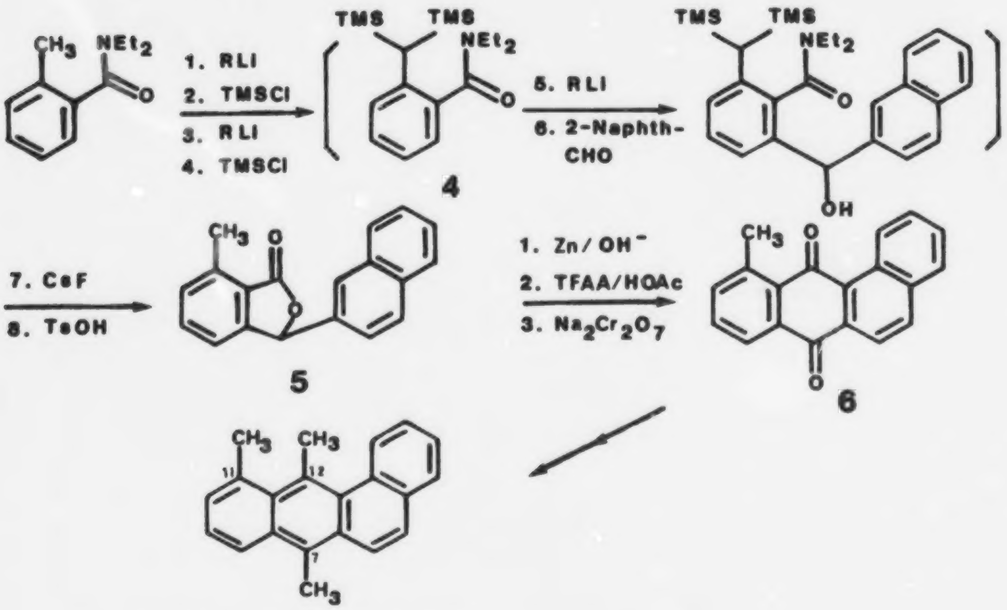
anthracene-9,10-dione
1-methyoxyanthracene-9,20-dione
2-methoxyanthracene-9,10-dione
benz[a]anthracene-7,12-dione
benz[b]anthracene-5,12-dione
dibenz[a,c]anthracene-9,14-dione
dibenz[a,h]anthracene-7,14-dione
dibenz[a,i]anthracene-7,14-dione
dibenz[b,i]anthracene-6,13-dione
naphtho[2,3-a]pyrene-9,14-dione
8-methyl-benz[a]anthracene-7,12-dione
11-methyl-benz[a]anthracene-7,12-dione
13-methyl-dibenz[a,c]anthracene-9,14-dione
benz[a]anthracene(BA)
benz[b]naphthacene
dibenz[a,c]anthracene
dibenz[a,h]anthracene
8-bromo-7,12-benz[a]anthraquinone
11-bromo-7,12-benz[a]anthraquinone
10-bromo-9,14-dibenz[a,c]anthraquinone
3'-bromonaphth-(2',3':3,4)-pyrene-1',4'-quinone

Aza-PAHs

benz[a]acridine
benz[c]acridine

Figure 3

Synthesis of Peri-Methyl Substituted PAHs


CH3
NEt2
O
1. RLi
2. TMSCl
3. RLi
4. TMSCl
TMS
TMS
NEt2
O
4
5. RLi
6. 2-Naphth-CHO
TMS
TMS
NEt2
O
OH
7. CsF
8. TsOH
CH3
O
O
5
1. Zn/OH⁻
2. TFAA/HOAc
3. Na2Cr2O7
CH3
O
O
6
CH3
CH3
11
12
7
CH3

7,11.,12-trimethylbemz[a]anthracene

Figure 4

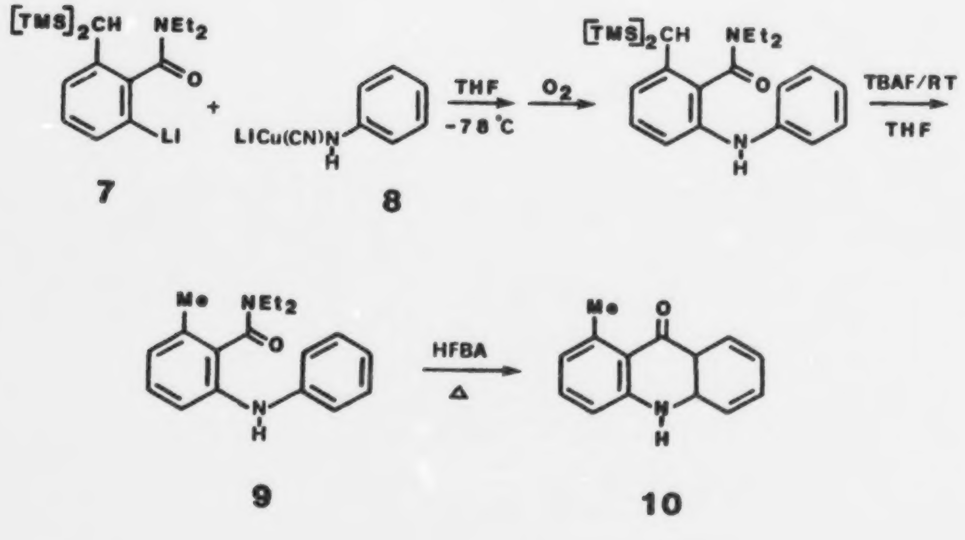
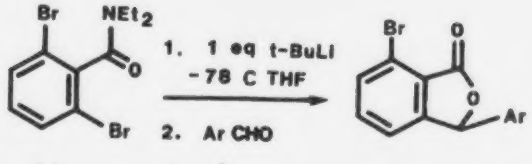

[TMS]2CH
NEt2
O
Li
7
+
LiCu(CN)N
H
8
THF
-78°C
O2
[TMS]2CH
NEt2
O
N
H
TBAF/RT
THF
Me
NEt2
O
N
H
9
HFBA
Δ
Me
O
N
H
10

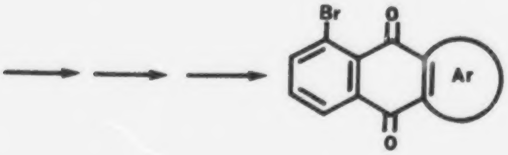
Figure 5

Synthesis of Bromo Substituted PAHs


Br
NEt2
O
1. 1 eq t-BuLi
-78 C THF
2. Ar CHO
3. H+
Br
Br
O
O
Ar

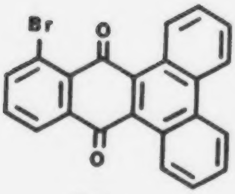
11

Ar = 1-Naphthyl **12**
2-Naphthyl **13**
1-Phenanthryl
1-Pyryl

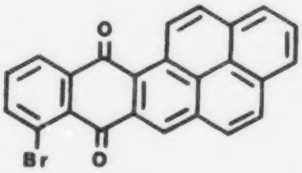


8-bromo-7,12-benz[a]anthraquinone **14**

11-bromo-7,12-benz[a]anthraquinone **15**



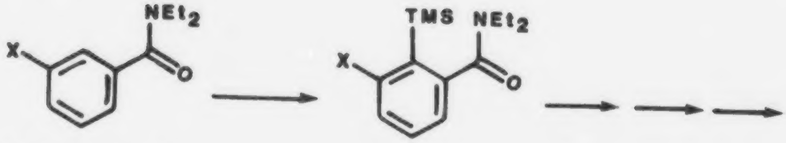
16



17

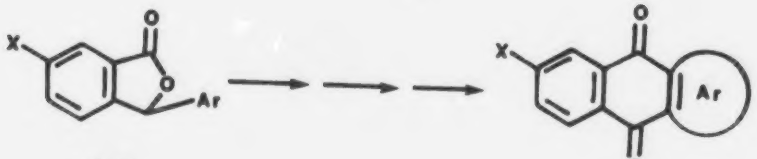
Figure 6

Synthesis of Chloro- and Fluoro-PAHs


NEt2
X
O
TMS
NEt2
X
O

18 X = Cl, F

19


O
X
O
Ar
O
X
Ar
O

20

21

Figure 7

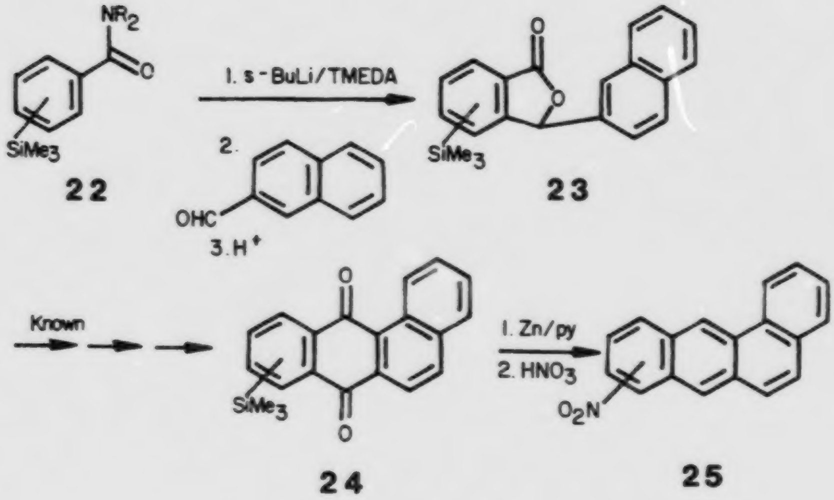
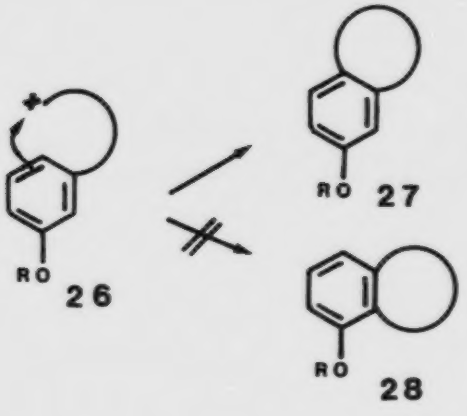

NR2
O
SiMe3
22
1. s-BuLi/TMEDA
2.
OHC
3. H+
O
O
SiMe3
23
Known
O
O
SiMe3
24
1. Zn/py
2. HNO3
O2N
25

Figure 8

Aromatic Electrophilic Substitution


+
RO
26
RO
27
RO
28

Normal Regioselectivity

Unfavoured Due to
Directing Effect
of -OR Substituent

Figure 9

Silicon-Directed Synthesis of 7-Methoxy-1-Indanols

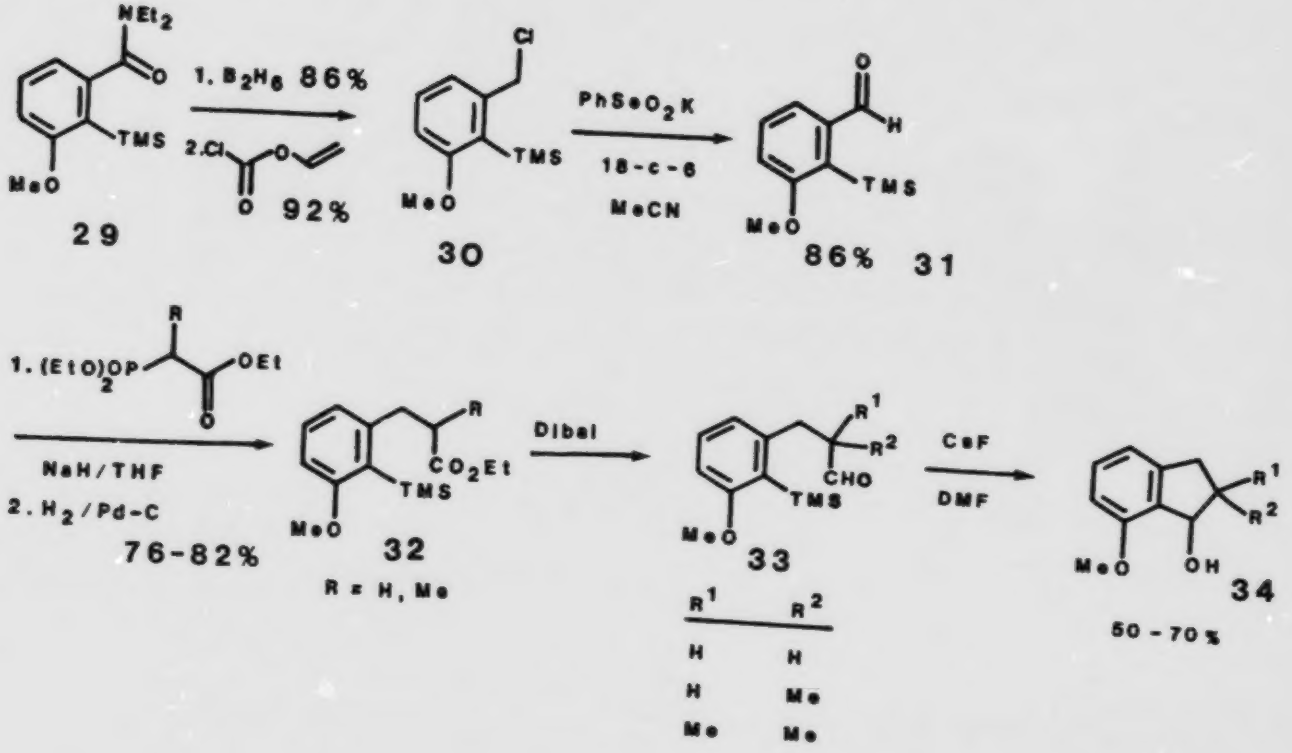

NEt2
TMS
MeO
29
1. B2H6 86%
2. Cl(CO)O-vinyl 92%
Cl
30
PhSeO2K
18-c-6
MeCN
H
86% 31
R
1. (EtO)2OP…OEt
NaH/THF
2. H2/Pd-C
76-82%
CO2Et
32
R = H, Me
Dibal
R1
R2
CHO
33
R1 R2
H H
H Me
Me Me
CsF
DMF
OH
34
50 - 70 %

Figure 10

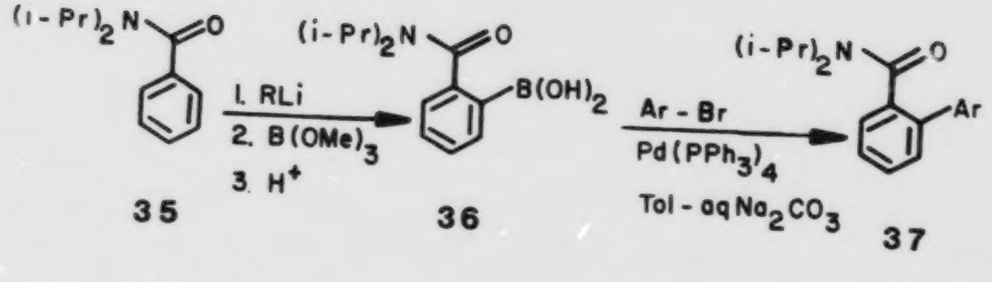

(i-Pr)2N
O
35
1. RLi
2. B(OMe)3
3. H+
B(OH)2
36
Ar - Br
Pd(PPh3)4
Tol - aq Na2CO3
Ar
37

Figure 11

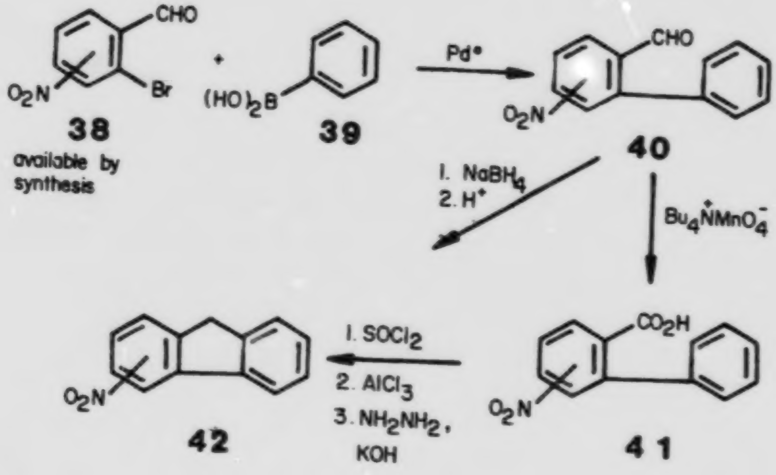
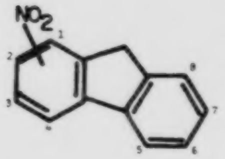
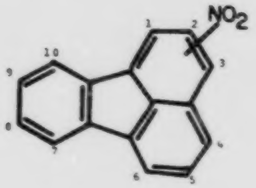

CHO
O2N
Br
38
available by synthesis
+
(HO)2B
39
Pd°
CHO
O2N
40
1. NaBH4
2. H+
Bu4N+MnO4-
CO2H
O2N
41
1. SOCl2
2. AlCl3
3. NH2NH2, KOH
O2N
42

Table **2**. Provision of Nitrofluorenes and Nitrofluoranthenes and their Hydroxylated Derivatives.


NO2
1
2
3
4
5
6
7
8


NO2
1
2
3
4
5
6
7
8
9
10

Nitrofluorene(F)

- $1\text{-}NO_2\text{-}F$
- $2\text{-}NO_2\text{-}F$
- $3\text{-}NO_2\text{-}F$
- $4\text{-}NO_2\text{-}F$

Metabolites/Oxid. Products:

- $1\text{-}NO_2\text{-}5\text{-}OH\text{-}F$
- $2\text{-}NO_2\text{-}5\text{-}OH\text{-}F$
- $3\text{-}NO_2\text{-}5\text{-}OH\text{-}F$
- $4\text{-}NO_2\text{-}5\text{-}OH\text{-}F$
- $1\text{-}NO_2\text{-}6\text{-}OH\text{-}F$*
- $2\text{-}NO_2\text{-}6\text{-}OH\text{-}F$*
- $3\text{-}NO_2\text{-}6\text{-}OH\text{-}F$*
- $4\text{-}NO_2\text{-}6\text{-}OH\text{-}F$*
- $1\text{-}NO_2\text{-}7\text{-}OH\text{-}F$
- $2\text{-}NO_2\text{-}7\text{-}OH\text{-}F$
- $3\text{-}NO_2\text{-}7\text{-}OH\text{-}F$
- $4\text{-}NO_2\text{-}7\text{-}OH\text{-}F$

Nitrofluoranthene (FA)

- $1\text{-}NO_2\text{-}FA$
- $2\text{-}NO_2\text{-}FA$
- $3\text{-}NO_2\text{-}FA$
- $7\text{-}NO_2\text{-}FA$
- $8\text{-}NO_2\text{-}FA$
- $9\text{-}NO_2\text{-}FA$
- $10\text{-}NO_2\text{-}FA$
- $3,7\text{-}diNO_2\text{-}FA$
- $3,8\text{-}diNO_2\text{-}FA$
- $3,9\text{-}diNO_2\text{-}FA$
- $3,10\text{-}diNO_2\text{-}FA$

Metabolites/Oxid. Products:

- $3\text{-}NO_2\text{-}6\text{-}OH\text{-}FA$
- $3\text{-}NO_2\text{-}8\text{-}OH\text{-}FA$(?)
- All isomeric 1-, 2-, 3-, and $4\text{-}NO_2\text{-}FA$ with 5-, 6-, and 7-OH available from corresponding $NO_2\text{-}OMe\text{-}F$ precursors.

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PROCEEDINGS

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December 8 & 9, 1986

The Sheraton Centre

External Research Projects

PART E
ENVIRONMENTAL ECONOMICS

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INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:
Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
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This part is a collation of those papers presented at Session E of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

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THE ROLE OF ECONOMICS IN ENVIRONMENTAL MANAGEMENT

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It is doubtful that there exists an area of public policy in which a clearer case can be made for the necessity of interdisciplinary approaches to problem analysis and policy design than the area of environmental quality management. Yet this case is regularly ignored on both sides of the line dividing economics from other relevant disciplines, including the life, chemical, and physical sciences, other social sciences, and certain of the humanities. It often seems as if each individual discipline is convinced it can tell society what its environmental goals ought to be and how those goals ought to be achieved. There is fault enough on all sides of this situation — and I certainly do not exempt my own discipline from that statement. But the purpose of this paper is not to apportion blame; rather it is to catalog the contributions that economics, in cooperation with other disciplines, can make to environmental policy. In the process, I shall indicate a few places where I believe economists have gone astray by failing to work with other specialities. But if a major message of this paper is intended to be a call to economists to cross disciplinary lines, I hope no one misses the flip side — it is equally silly for engineers or biologists or medical doctors to think that they have a singular hold on social welfare and that economists should only be called in at the end, to estimate the costs of the proposed policy and judge whether or not firms "can afford it."

Indeed, it is worth making one more preferatory point, obvious to some, perhaps heretical to others. None of the scholarly disciplines, alone or in combination, can tell society what it ought to want by way of an environmental quality goal, or even by way of management techniques to obtain a given goal. The most we can do is to point out the implications of a variety of possible choices of goals and management techniques, including implications for all parts of the environment; for costs, international competitiveness and job displacement; for health and comfort; for the value of recreation; for our self-image as a society; and so on.

All that said, let me proceed to a brief catalog of the potential contributions of economics. I believe that those contributions may be subsumed within three broad areas:

- critically examining often conflicting claims about the need for any government policy (or conversely, about the desirability of "deregulation")
- estimating the costs and benefits associated with and predicting the indirect effects of particular policies -- either before or after implementation — as an input to the decision process
- analyzing implementation problems, and designing positive and negative incentive systems, and accompanying monitoring and enforcement activities.

The Need for Public Policy

It is worth starting here because our democratic societies seem to swing with alarming rapidity between two extreme views. One is if we find anything at all not to our liking, government regulation must be the answer. The other is that any perceived social problem can be solved by some ingenious definition of rights and creation of a market in those rights. The best role for the economist, in my opinion, is that of skeptic, demanding that the would-be regulator make a technical case for intervention; and being equally tough on the marketeer, asking for the reasoning that makes him or her think a market can work.

That role as skeptic is founded on some powerful welfare theorems based on strong assumptions, and on trenchant analysis of when the assumptions can be expected to be invalid -- when the theorems should fail. The relevant theorem for environmental policy concerns says that, in the absence of complications, the competitive market reflecting the optimizing behavior of individual consumers and producers can lead to a situation in which no one can be made better off without someone else being made worse off -- a Pareto optimum in the jargon of the trade. This result, the "invisible hand" of Adam Smith, rests on the existence of prices for goods, services, land and savings, that are faced equally by all participants in the market and that carry, in remarkably efficient summary form, information about the desires of individuals and capabilities of technology. Economists with a keen appreciation for the difficulty of obtaining and transferring that information in ways dependent on a central agency, begin with a predisposition to opt for markets where opting is possible.

But what are the "complications" referred to above? Again, confining myself to matters most germane to environmental management, I will concentrate on one: the existence of public goods. Such goods are those like sunsets, national defense, and ambient air quality, that we all share willy nilly. My consumption -- as a viewer of a sunset, a protected citizen, a breather of air -- does not, in the normal course of events -- interfere with your consumption of the same amount of each public good. Two of us or two hundred or two hundred thousand can all consume the same sunset, the same security and the same air quality (the latter with qualifications that need not detain us). Indeed, it is difficult, if not truly impossible, to prevent those resident in the area in question from enjoying a sunset, breathing the same quality air, and so forth.

Public goods need not be free; national defense costs money. They need not be provided by the government; a fireworks display involving rockets provides a public good to people away from the site at which the rockets are touched off and to which admission might reasonably be rationed by a private person or firm. Nor are all government-provided goods public in this technical sense. The Post Office provides an intrinsically private service which I can easily be prohibited from enjoying if I don't pay.

The problem with public goods is that the decentralized price system cannot deal with them. If we could calculate the optimum amount of air quality in a region, we could not obtain a price to charge potential consumers of the good that would make each person desire to consume just that optimum amount. In principle, we could obtain, by dint of great effort, individualized prices so that each individual would be charged a price consistent with him or her wanting the socially optimal quantity. But of course it is difficult in any case to charge a price, individualized or common, for a public good. In summary, the price system, and hence the market, fail "by existence", as a great expositor of these results put it.

Thus, if the "invisible hand" welfare theorem gives economists a predisposition to favor market solutions, the existence of public goods in such policy areas as environmental quality should give them pause in recommending market-like solutions to environmental problems. For example, consider the suggestion that we should simply define marketable permits to discharge pollution, thus creating property rights to be traded, and let the resulting market determine environmental quality. Those who want higher quality (lower discharges) than provided for in the initial offering of rights can, it is claimed, combine to purchase and retain rights. Aside from technical problems having to do with possible concentration of rights on a few hands resulting both in cartel-like price power and environmental "hot spots", the prescription deserves intense skepticism because no sub-group of individuals can either determine or pay for the socially optimal amount of pollution control.[1] Such a system would not be adjustable in the higher quality direction except by further government intervention. Similarly, privatizing wilderness makes no sense so long as the public good, knowledge of wilderness preservation, has value to non-users of wilderness areas.

There should be no need to belabor the point: economists have tools available for evaluating arguments about and prescriptions for government intervention in or private market solutions to environmental problems. In their analysis they will be informed by other specialists such as atmospheric and aquatic scientists and even psychologists, who can illuminate the conditions determining whether particular environmental services are public goods or not.

THE COSTS, BENEFITS AND RELATED EFFECTS OF PROPOSED POLICIES

While public goods foul up markets, they are still worth something to consumers of them. The trick is to find out how much those consumers would be willing to pay for environmental improvements. Environmental public goods, such as improvements in air quality, cost something, in real resource terms too. And while cost estimation is generally agreed to be conceptually easier than benefit estimation, it is by no means trivial, especially not when what is being costed is a change in ambient environmental quality.

[1] It is worth pointing out that pollution discharge is conceptually a private good, access to which can be priced and rationed so that a desired total amount can be achieved through a common price applied to all dischargers. On the other hand, the spatial distribution of discharges is, in general, germane to the ambient quality level experienced at different points in a region, so to obtain a given spatial distribution of desired quantities, discharger-specific prices are required. Further, the ambient quality produced by the combination of discharges and natural environmental action, is a public good. Citizens, as consumers of air quality, not discharges, have to deal with the public good problem.

Other effects not captured by resource costs or estimated willingness to pay may be important to policy makers as well. For example, displacement of jobs from high sulfur coal mining in one region to low sulfur coal mining in another region has been a vexing dimension of SO_2 emission control policy in the U.S. Economists can provide information in all these areas with suitable cooperation from other disciplines.

This is clearest in the case of benefit estimation, so let me concentrate on that problem and leave the others with the brief assertions of the previous paragraph. But first, let me observe three things. One: even if aggregate and marginal costs and benefits could be perfectly estimated, that would not say that benefit-cost analysis should be the basis for social decision-making about environmental quality or anything else. There are deep ethical questions here about how to deal with individual welfare in the absence of actual payment of compensation; and the benefit-cost criterion is but one answer. More to the point in actual decision-making, political reality involves complex balancing of group interests in the presence of inflexibility in the distribution of both benefits and costs. That means cost-benefit analysis can never be more than one input to the process.[2]

Two: I am not claiming that benefit estimation is even a necessary part of environmental policy-making. If society collectively decides that benefit estimation should not be done, it is certainly possible to make policy on the basis of discussions about costs and physical effects -- ambient concentration changes, visibility improvements, fish population changes -- and costs. This does tend to result in each regulator and politician supplying his or her own ad hoc estimate of benefits, but that is ultimately what politics requires anyway.

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[2] It is a required input now in the U.S. under President Reagan's Executive Order 12291, which requires the preparation of C-B analyses for all major regulatory decisions, even where the existing legislation says that such analyses can play no role in the decision.

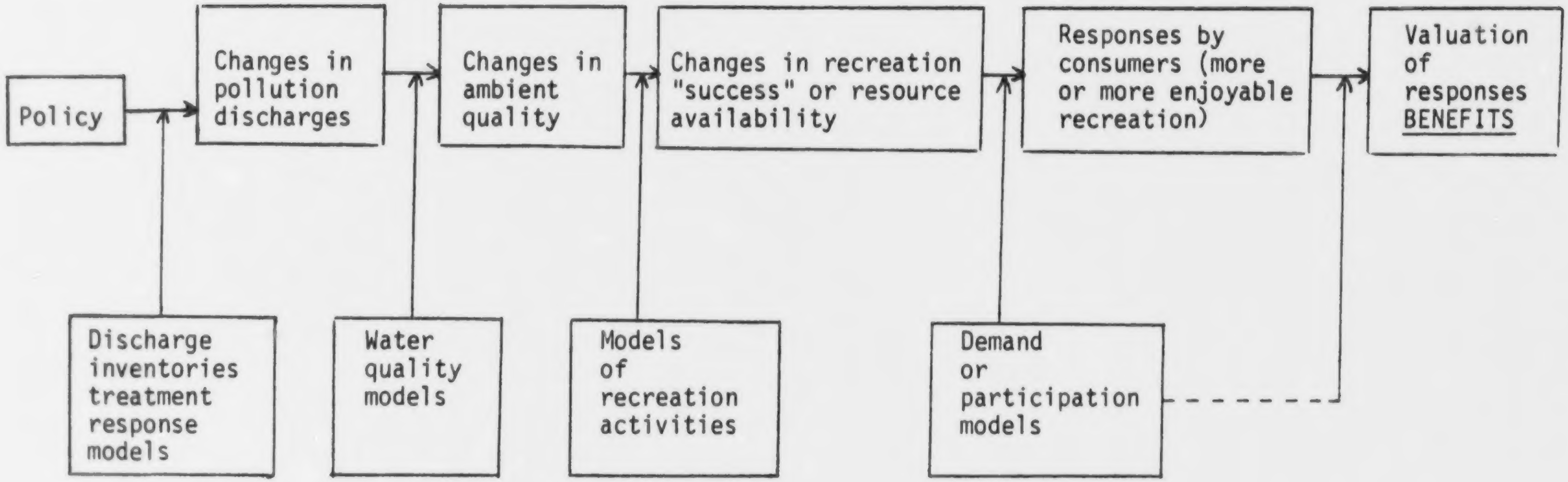
And three: I believe that in the current state of the art, we can supply only highly aggregated and imprecise estimates for part of the benefits of any particular environmental policy. But what we can accomplish today is vastly more than we could accomplish 10 years ago. With wise investment of research and development funding I believe we could see as much improvement again in the next 10 years. By 2000, benefit estimation for environmental policymaking may be worthy of being taken quite seriously indeed.

To see why benefit estimation is hard, it is necessary to understand what is involved in doing it. One way of setting out such an understanding is in terms of "linkages" -- those connections between the parts of the puzzle necessary to turning a particular policy description into a benefit number (or range of numbers, more properly).

As one among many possible examples, let me describe the set of linkages for understanding water-based recreation benefits. This is laid out schematically in figure 1. Notice that we must know about pre-policy discharges and how they will change; what these changes in discharge levels will do to water quality; how the "objective" changes in water quality are viewed by different categories of recreationists; how those views translate into responses in the sense of leading to more or less enjoyable activity; and how these changes in recreation behavior are valued.

This is a formidable menu of "musts", and it turns out that in every case we lack the data and models to do the job as it should be done. The following is a brief description of what is and is not available.

FIGURE 1
From Policy to Benefits:
Linkages to be Understood


Policy
Changes in pollution discharges
Changes in ambient quality
Changes in recreation "success" or resource availability
Responses by consumers (more or more enjoyable recreation)
Valuation of responses BENEFITS
Discharge inventories treatment response models
Water quality models
Models of recreation activities
Demand or participation models

For discharges we have perhaps the best information; yet it displays large elements of approximation and inference. A massive point source inventory that exists at Resources for the Future (RFF) has been extended to include inferred loads of nonpoint pollutants from various source categories. This is a version of an inventory maintained by the U.S. Environment Protection Agency (EPA). But even this inventory is based in large part on rules of thumb rather than measurement.

Predicting how the policy will change discharges is sometimes easy, sometimes difficult. The easiest policy to deal with is one of required percentage reductions; the hardest -- that applying to soil erosion, for example -- is one based on "best management practices" where the results cannot be precisely estimated. In between lie the technology-based point source standards, such as "best available technology," which are translated into discharge requirements by reference to model or average plants in particular categories. (Such projections for point sources are possible in the RFF inventory referenced above.)

Estimating how discharges affect water quality and how quality affects recreation is difficult given the state of the art in natural systems modeling. As a practical matter, estimates are often restricted to the relationship between biodegradable material and instream dissolved oxygen (DO) levels. There are two problems here: one is predicting how the aquatic system will react to pollutants in any terms. The second is finding measures that relate both to discharges and to recreation. For example, DO is one indicator we can link back to discharges, and it can be linked forward to fish survivability, clearly relevant to recreational fishing benefits. But DO is not, except at its extreme low end, linked well to boating or swimming decisions. The appropriate indicators for these activities may include turbidity, oil and grease, microorganism counts, and floating solids. These indicators are not now routinely predictable with acceptable confidence by state-of-the-art water quality models acting on discharges. Thus, benefit estimation waits on work by sanitary engineers and aquatic biologists on improved water quality predictive models.

Benefits are generated when consumers get increased enjoyment from the same spending (of time and money), spend less for the same enjoyment levels, or spend more and obtain more. The problem here is that these responses are not, in the natural course of things, recorded; nor are these changes linked in any easily recordable way to particular changes in water quality. To illustrate these points, if one French restaurant in a city changes its menu or decor or chef, the results, if there were any, would be recorded in its sales volume and number of meals served. (Enhanced enjoyment per meal would not be recorded. Only if higher prices could be charged and the same volume maintained could we infer such an effect. Otherwise, direct interviews would be necessary to acquire such information.) In another example, if the Potomac River just above Washington were clearer on average throughout the year, there would likely be an adjustment by area fishermen to substitute the Potomac for more distant waters or increase the frequency of their outings or just enjoy each Potomac outing more. None of these effects would be observed, however, without a substantial special data-gathering exercise.

Even when some special effort is made to gather data on what recreationists do, the assembled information typically does not include the prices recreationists are paying to do these things. The actual recreation experience is usually unpriced, and what people pay is largely bound up in necessary complementary goods, such as boats for boating, or spent in the form of travel costs (direct and travel time values).

In these circumstances, values attached to changes in recreation-related water quality must almost always be inferred from indirect evidence. In the best possible situation, data would be available for individuals on the set of travel cost prices for alternative sites, the activities facing each, and the resulting "purchase" of activity days by place and activity. These data would, of course, be in addition to the usual income and related data. From these data, demand functions for days of the activity would be estimatable. Such functions would immediately yield well understood approximations of the benefits of changes in the set of travel cost prices implied by increases in availability of activities due to pollution discharge reduction.

More commonly, the best that is available are data on participation by individuals in the activities of interest without either travel cost prices for possible places or information on where the individuals actually did go. Work on recreational fishing benefits generally reflects these limitations.

It is possible to approximate average (or expected) travel cost by using an inverse function of the density of suitable — including suitability by virtue of being unpolluted — water areas. An average travel cost proxy can then be attributed to each individual for a region or jurisdiction, with participation being related to this and other variables. Changes in participation because of changes in availability, due in turn to discharge reductions from pollution control, can then be projected. Because the real travel cost prices are not available, the money welfare measure (the benefit) of changes in behavior does not fall directly out of what is estimated. Rather, a two-stage process must be used: first, projecting changing participation in, say, activity days; and second, producing separately a value per day, perhaps from a completely different source. The pitfalls of such a strategy have been described elsewhere. Suffice it to say here that simulation studies show that such a method can give results that are off by more than 100 percent or can, on the other hand, comport very well with the "true" results. Unfortunately, in real cases, we cannot know which situation applies.

Other methods of benefit inference are also possible, including one based on the purchase of complementary goods. In boating, for example, data on ownership is the most extensive and detailed available; data on boating activity exists only for much smaller samples. It must be stressed that in all actual cases of indirect inference, we face data that are substantially poorer than those required for the "best" situation. In particular, in no case I know of have the necessary travel cost prices been available. Beyond that, the quality of the price proxies is bound to be suspect because of the dearth of even baseline data on water quality in recreation-related terms. For example, in a recent study of the pollution control benefits accruing via swimming, boating, and marine recreational fishing, the analysis had to fall back on a survey of state officials that asked for their judgments about the extent to which water areas were unavailable due to pollution.

Thus, at the heart of the benefit estimation procedure are several data gaps that are expensive to plug, have not been plugged in the past, and are unlikely to be in the future. The upshot is that as a practical matter we can have only limited faith in the results of "classical" recreation benefit studies, even when the policy being considered comprises all pollution control activities.

There is an alternative to part of the tricky chain of inference set out above. This is the direct, or willingness-to-pay-survey, or contingent valuation technique. As the several names suggest, the method amounts to asking people what they would be willing to pay for specified changes in the level of environmental services (public goods, remember) connected to particular policies. Economists have traditionally turned their noses up at this method because of the incentives people can be shown to have to misrepresent their preferences. But recent research seems to me to show that these incentives are not important enough in the survey setting to make it worthwhile for people to think through the complicated problem of how they ought to lie. It is easier to try to tell the truth. In the long-run this method of obtaining directly estimates of willingness to pay seems to me to be the most promising item in the benefit estimation armory. But in the context of this paper's stress on the multidisciplinary character of the environmental problem it is worth noting that this method requires much non-economic input. None of the linkage in figure 1 except the last is really avoided by using contingent valuation methods, if we want to ask reasonable questions linked in meaningful ways to real policy alternatives. In addition, the art of designing surveys is one in which economists are not normally trained. They need help from disciplines such as sociology and psychology if they are to have survey instruments that have any real chance of producing what is intended.

Implementation of Environmental Policy

This is an area in which a tremendous amount of ink has been spilled by economists over the years. Because of the disciplinary fascination with decentralized prices and market efficiency, there have been a series of attempts to show how an administered price system (effluent or emission charges) could solve all, or at least a good part of, society's environmental problems. This ingenuity has also been directed to the idea of marketable permits to pollute. Most recently, economists have taken an interest in monitoring and enforcement as a part of whatever implementation scheme is adopted.

While I am critical of the classical literature in this corner of environmental economics, I believe useful contributions have been and in the future can be made by economists if they are careful to inform themselves of the relevant technical features of the problem. Thus, the early fascination with uniform emission charges followed from a grounding in classical economic theory without a corresponding appreciation for the importance of location in determining a source's contribution to a regional environmental quality problem. As pointed out above, when location differences are taken into account, uniform charges cannot be used to achieve static economic efficiency (least cost for given ambient results). Indeed, it can be shown that they are not even the best of the second best implementation methods.

But later analyses of implementation have not only recognized the technical problem raised by different source locations in a complex environment, but have also gone beyond static efficiency considerations to take into account a wider area of criteria for judgment. For example, it has been recognized that such criteria as the following are relevant:

- Flexibility in the face of a changing economy. Thus, administered prices must in principle at least be recalculated when anything changes -- an old source is shut down or a new one opens, a process change occurs that lowers one source's marginal abatement curve -- if static efficiency is to be maintained beyond the initial period.
- Dynamic incentives. Economists have shown how "ratcheting down" of discharge standards as technology improves, as provided for in U.S. water pollution control legislation, can destroy the incentive for undertaking research aimed at that improvement. Thus, far from aiming the system at zero discharge, ratcheting down may condemn it to stagnation with existing technology.

- Consistency of monitoring and enforcement capabilities with implementation scheme design. Thus, for example, if we regulate or charge for discharges per unit time, we must be able to measure such discharges and have a means to do so often enough and precisely enough to present the source with a credible threat of being found in violation if actually violating permit terms or cheating on charge payments.

The last point, on monitoring and enforcement, deserves special emphasis because in the past economists have done so little with it. For the most part, the literature on charges and standards has assumed compliance and derived the static economic implications of that assumption under the different instruments of policy. But a discipline based on an assumption that actors pursue their self-interest could hardly be content with assuming costly compliance would occur. As one examines the alternative in any particular situation, it becomes clear that useful advice requires knowledge of the applicable law, of available measurement technologies, and of statistical tools for deciding when a violation has occured. Further, environmental problems differ in the character of the polluting act and hence in the nature of monitoring. Keeping track of the discharge of SO_2 from a smokestack in a known and fixed location is one thing. Making sure that barrels of spent dry cleaning fluid end up in the right place and not in the woods is quite another. In the one case a marketable permit might have many advantages; in the other a positive incentive such as that provided by a deposit-refund system might be more to the point.

Thus, technical knowledge of specific environmental problems must go hand in hand with economic ideas about incentives for static efficiency and dynamic change and with recognition of the administrative costs of inflexibility.

Over all, the design process can usefully be informed by ethicists and political scientists, who can analyze and sometimes help to mitigate features that are political liabilities.

Concluding Comment

This has been a selective survey of the potential contributions of economists to the ongoing debate about environmental policy — choice of goals as well as of implementation methods. The message I hope the reader will take away is that these contributions are substantial and socially valuable but that economists will never reach that potential operating alone. Only in the context of multidisciplinary approaches can their insights and tools be really useful.

ABATEMENT COST FUNCTIONS

THE "WORKHORSE" OF ENVIRONMENTAL MANAGEMENT

BY

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POLICY AND PLANNING BRANCH
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ABATEMENT COST FUNCTIONS - THE "WORKHORSE" OF ENVIRONMENTAL MANAGEMENT

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1. Introduction

To many people, environmental economics primarily concerns two issues: the cost of environmental protection activities and whether such costs will have severe economic repercussions on employment or on particular firms, industrial sectors or regional economic activity. Media reports about environmental affairs invariably cite cost estimates of proposed abatement programs with little explantation or qualification. Such cost estimates are often obtained from firms which are faced with abatement requirements and who may claim that compliance costs will cause severe economic disruptions. In such instances, cost estimates are sometimes overstated and so must be verified.

On the other hand, environmental criteria and guidelines have sometimes been promulgated without explicit consideration of the costs of achieving them. Environmental requirements of this nature, as well as technology-based abatement objectives such as "best available technology," imply that unlimited amounts of money should be devoted to pollution control and environmental protection.

In a society that must satisfy its needs from limited resources, one cannot devote all available funds to a single purpose. Procedures and criteria must be established to allocate available money and efforts among competing uses in order to produce the range of goods and services (including free public goods) that are most desired and valued by society at large. However, in order to allocate funds efficiently and fairly to environmental protection activities, information about the costs of achieving different requirements and objectives is absolutely essential.

Moreover, properly defined and delineated cost data, or estimates of expected costs, are essential for making informed and rational choices concerning environmental policies, programs and abatement activities. Such information can be used in a variety of ways to design programs, predict reactions to regulatory initiatives, assess impacts and to set environmental objectives

Dewees (December 1976) discusses the kinds of abatement cost data or estimates that are needed for effective decision-making with respect to environmental production activities . He argues that the best information one could have would be a schedule of costs to achieve all conceivable levels of emission controls for any given industrial plant or polluter.

Estimates of the range of costs that would be incurred to achieve different levels of emission reduction are far more useful for policy deliberations than single-valued cost figures. These ranges of costs, together with their associated emission reductions (or final emission levels), are called abatement cost functions. Because there are so many analytical techniques, issues and questions that require this information or that can be assessed by it, abatement cost functions can truly be called the "Workhorse" of environmental economics.

The purpose of this paper is to review some efforts here in Ontario that have been made to generate and use the kind of cost data or estimates suggested by Dewees. In doing this, the key theoretical concepts that define abatement cost functions will first be reviewed. The functional forms in which abatement cost information can be presented will be discussed along with an explanation of how abatement costs functions are related to traditional production cost functions.

Methods and approaches for deriving empirical abatement cost functions will then be catalogued. A set of computer programs which was developed by staff at the Ontario Ministry of the Environment, and which can be used to generate empirical cost function information, will be described briefly.

Several specific examples will be cited which illustrate how empirical abatement cost functions have been derived and how they might contribute to Ministry of the Environment regulatory choices and decisions. These example will highlight specific uses that can be made of this information including determination of least-cost abatement programs for specific polluters, setting defensible environmental objectives, making explicit environmental-economic trade-offs, assessing financial impacts on firms who are subject to abatement requirements, evaluating the consequences of different enforcement policies, anticipating the reaction of a firm or a municipality to abatement requirements and the development of "affordable" abatement programs and schedules for specific polluting establishments.

The paper will conclude with some comments about the availability and accuracy of data needed to generate abatement cost functions together with some suggestions as to how to assemble these data. Further research and applications of abatement cost analyses in the Ontario context will also be noted.

2. Production and Cost Functions - Theory and Concepts

Individuals strive to maximize their satisfaction or utility from the goods and services which they buy or use (including free public goods). Firms endeavour to maximize profits from the goods and services they sell. In its simplest form, profit is equal to revenues less costs. In a competetative market economy where prices are determined exogenously, firms generally only have control over their costs. Similarly, public agencies and governments usually have less control over their revenues than they do their costs. Consequently, both public and private agencies make efforts to minimize their costs in order to achieve cost-effective operations and (in the case of private firms) maximize profits. Information and data on the cost are, therefore, critical to the effective and efficient operation of an agency or an enterprise.

Costs are generally perceived to be the value of the inputs used in a productive process or activity. These inputs include the raw materials, machinery, equipment, labour, energy, interest, administration and, for private individuals or companies, a minimum return on investment. These **accounting costs** are compared with outputs or revenues and are used to make production and investment decisions. Market prices and wage rates of the various inputs generally provide reliable measures of their value to society.

However, costs should be viewed in a much wider context. When resources or inputs are put to certain uses, the benefits they could yield in other uses or applications are irretreivably lost. Opportunities to produce other goods or services or to gain other kinds of utility and satisfaction are foregone. Consequently, economists refer to the **opportunity costs** of producing goods or implementing a project. The distinction between accounting and opportunity costs is important in certain circumstances. For example, some foregone benefits or opportunities, such as swimming or recreational fishing that may be precluded by pollution, are not normally marketed so that prices are not available to determine their value. Although those who cause pollution do not have to bear these social costs, their private accounting costs are less than the total opportunity costs of the polluting activity to society. Opportunity costs may also diverge from accounting costs when there is substantial unemployment or when there is monopoly pricing of factor inputs.

In its efforts to minimize costs and maximize profits, a firm must face two key questions:

- how much output should be produced?
- what combination of inputs should be used to produce any given quantity of output?

The level of output is determined by comparing the prevailing market price with the incremental or **marginal cost** of producing extra units of output. Marginal cost is defined below. Profit is maximized when a firm produces output so that the marginal cost of the last unit of output is just equal to the market price or the extra revenue it receives from the same unit of output.

The second question is answered by mixing inputs so that the largest amount of output is produced at the lowest cost possible. This is accomplshed by following a relatively simple rule. Costs of producing given levels of output are minimized when the ratios of the extra output of each unit of input (eg. labour, raw material etc.) to the price of the input are equal. This rule is also satisfied when the marginal costs of each input factor are equal. This test is easier said than done but it provides a rule for cost minimization that can be applied to any sort of production process for which appropriate cost data are available.

The extra output that can be produced with an extra unit of any of the necessary inputs is determined by means of a production function. This is nothing more than a schedule of outputs that can be produced by specified quantities of variable inputs.

The accounting costs to which an enterprise (or for that matter a government agency) is subject include **fixed costs** and **variable costs**. Fixed costs are those expenses that must be incurred whether or not something is being produced. Variable costs are the quantities of variable inputs (eg. labour, raw materials, etc.) times their unit prices.

Three different cost measures are generated and used in cost analyses:

- **Total cost** = total fixed plus total variable costs for a specified quantity of output.

- **Average cost** = total cost divided by quantity of output.

- **Marginal cost** = increase (or decrease) in total cost divided by the increase (or decrease) in output. This is the same as the change in total cost resulting from an increase or decrease in output by one unit.

The production function specifies the physical quantities of inputs needed to produce an output. Cost functions convert these physical quantities to measures of monetary value such as dollars per unit time or net present value terms.

It is exceedingly rare that there is only a single technical option or level of effort that can be applied in a particular pollution situation. Consequently, there is a generally a range of different levels of pollution control or environmental protection that can be achieved at different costs. For any given level of abatement or final emissions, there is one combination of technologies or options that is least-cost. It is understood that an abatement cost function consists of only those least-cost points.

In general, costs increase with increasing degrees of abatement (or declining levels of emissions or "pollution intensity"). The relationships between total abatement costs and final emissions and between marginal costs of abatement and final emissions are depicted in Figure 1. These relationships are contingent upon existing technologies and their compatabilities for combination. This particular functional form also assumes a constant design capacity for the particular technologies.

Figure 1 implies that total costs of abatement increase gradually over a particular range of final emissions. As one attempts to remove the final quantities of contaminants or emissions, costs rise rapidly to the limits of the available technology. Marginal costs, which are the first derivative of the total cost function, are zero when total costs do not change; constant at some positive amount when total costs increase at a constant rate; and rise when total costs increase at an increasing rate. Information about the shapes of the marginal and total cost curves for a particular pollution source can be extremely useful to the assessment of an abatement program and the design of appropriate objectives and policies to achieve them. Dewees, Everson and Sims (1975: 80-90) analyse these relationships as well as relevant optimization conditions in some depth.

A cost function alone does not provide sufficient information to determine a socially desirable emission limit or objective (however this might be defined). Other information such as discharge or ambient concentration objectives or the value of the benefits of different levels of final emissions would be needed to make such choices. For example, in order to achieve a level of pollution control that is broadly "efficient", abatement should proceed to the point where the value of the extra (eg. marginal) benefits are just equal to the relevant marginal costs.

Cost functions can, however, be used to determine the least expensive combinations of controls and abatement when there are two or more sources at a given location and the resulting emissions are perfectly mixed so that they do not cause differential effects (Dewees, Everson and Sims, 1975:20-24). Abatement is achieved at the lowest overall cost when each source controls its emissions to the extent that their marginal costs of abatement are equal (Dewees, Everson and Sims, 1975:29-31; Downing, 1984:76-79). This is analogous to the marginal condition for minimizing production costs in a firm noted earlier.

The concept of equating marginal costs and benefits is useful even in cases where neither benefit nor cost curves are precisely specified. Estimates of a few points on either curve, or even general ideas of shapes and magnitudes, can help design rational policies and programs (Dewees, December 1976:6). In fact, one could interpret the "best available technology" requirement as economically efficient if marginal benefits were reasonably constant over a wide range of abatement and if the "best available technology" is interpreted as lying just below the sharply rising portion of the marginal cost curve.

3. Empirical Estimation Procedures

Empirical studies of abatement costs are invariably restricted to accounting cost items. The cost catagories generally consist of capital in vestment, operation and maintenance (O&M), interest or capital charges and, in some cases, land and installation charges. Capital costs, land and installation charges are one-time costs whereas O&M and interest are recurring costs, generally on an annual basis. These capital and O&M costs are incommensurate measures and cannot be legitimately summed. In many instances, only capital costs are cited. But annual O&M and other costs can constitute a significant proportion of the total costs incurred over the life of an abatement system.

If O&M and other annual charges are expected to be constant (other than for inflation) over the life of the system, then capital costs can be "annualized" with an appropriate amortization algorithm and added to O&M to yield a typical or average annual cost. This figure can then be compared with similar estimates of other systems or options. If O&M costs are expected to change significantly over the life of the system or if new equipment will have to be installed during the planning period in question, then future costs are discounted and summed together with the initial capital expenditure to yield a net present value (NPV) which can also be compared with estimates for other options or systems.

Empirical abatement cost functions can be divided into three methodological groupings (Dewees, Everson and Sims, 1975:94). **Engineering studies** define in detail the necessary equipment and related costs for a particular technology or to achieve specified abatement objectives. This approach is often the source of single-valued cost estimates. The second method utilizes **statistical or econometric** techniques. Equations are identified and estimated using data on existing facilities to estimate coefficients with linear regression techniques. The third method, termed the **systems analysis** approach, attempts to combine all feasible abatement technologies and systems in a programming framework to determine the least-cost set of abatement programs.

Over the past 10 years, personnel in the Ontario Ministry of the Environment have developed a set of computer programs which can be used to generate empirical abatement cost functions for ranges of abatement levels at individual industrial plants. Called the **WAste Treatment Analysis Program** (WATAP), it best classified as a "systems analysis" technique. WATAP consists of two "Steps." "Step 1" is a program which will:

- identify all combinations of treatment technologies that can be implemented at a plant. Each combination of one or more technologies is called a **Plan**;

- incorporate specified technical incompatibilities so that only those combinations of technologies that are technically feasible are specified.

Step 2 consists of a set of programs which use the results from Step 1, plus other data, to:

- calculate the expected reductions in each pollution parameter, the final emissions and the timing of these reductions, for each Plan;

- calculate the capital and the total net present value of all costs and revenues associated with each abatement Plan over a user-specified planning period (eg. 20 years);

- calculate the effects of each Plan on the company's cash flow and the Provincial Government's tax receipts;

- calculate the cost per unit of emissions removed or reduced.

Step 2 can also sort the feasible Plans, of which several hundred may be identified for a single industrial plant, from lowest to highest emissions or from lowest to highest cost. The WATAP can also extract the set of Plans which will achieve successively lower levels of emission reduction at the lowest cost (or highest net revenue). This is the least-cost set of Plans and constitutes an abatement cost function.

Each Plan is independent of each other. Thus, in order to achieve a specific reduction in emissions, one would implement the least-cost Plan that would achieve the desired reduction. However, one cannot subsequently "add on" another Plan in order to reduce emissions further. The treatment technologies that make up each Plan can, however, be implemented consecutively or concurrently.

The WATAP uses plant-specific data concerning pollutant loadings at each outlet, abatement technologies, abatement efficiencies, costs and compatibilities among technologies. Various kinds of economic and interest rate data are also required.

The WATAP generates a net present value estimate for each Plan over the user-specified planning period. Because costs and revenues are escalated each year to reflect inflation and any expected changes in relative prices of inputs or recovered by-products, nominal rather than real interest rates are used in discounting and in calculating loan interest payments.

The relevant cost and final emissions estimates from the least cost set of Plans is a total cost function. Theoretically specified marginal costs cannot be calculated from WATAP estimates. However, an average cost per unit of pollutant removed can be calculated which can be used to compare abatement Plans and costs among different plants. Since the present value figure that is used as the numerator in the ratio is based on costs (and revenues, if any) over the entire planning period, the reduction in emissions that is achieved over the same period should then be used as the denominator in the ratio. Moreover, this ratio can be calculated only on the basis of one emission parameter at a time. Comparisons of these ratios can indicate which of several plants can reduce its emissions at the lowest cost.

Some of the input data and assumptions made in specific applications are often uncertain. For example, treatment efficiencies could be higher or lower than those used in the analysis. Moreover, cost estimates for each treatment technology could be higher than anticipated. Using the WATAP, re-estimations of the costs and emission reductions resulting from each Plan can be made with different input data or assumptions.

In the sections to follow, applications of the WATAP and other techniques will show how empirical abatement cost functions have been generated and how this information has been used to conduct various types of analyses and assessments that may be required in regulatory decision-making.

4. Empirical Abatement Cost Studies in Ontario

4.1. Inco-Falconbridge Task Force

In May of 1980, an Ontario/Canada Task Force was established to investigate and evaluate air pollution (especially sulphur dioxide or SO_2) abatement technologies and options for the nickel and copper smelters operated by INCO Ltd. and Falconbridge Nickel Mines Ltd. in Sudbury. Sulphur emissions have been a long-standing problem from these sources and, while steady reductions in total emissions had greatly improved the ambient air quality conditions in and around Sudbury, further reductions were thought to be required to address the long range acid depostion problem.

Although provincial SO_2 emission reduction targets had not been established at that time, it was nevertheless recognized that any commitment to reducing acid deposition must include abatement at the Sudbury smelters.

Absence of specific emission targets for the smelters in the Sudbury area, together with the large number of possible abatement technologies that could be implemented by these sources, made the analysis of potential process changes and abatement programs a formidable task. Even when the technologies to be considered were limited to those which would require no more that five years of development work to determine their effectiveness, hundreds of potential permutations and combinations of technologies were possible. Moreover, even when potential programs were identified, it was not clear which ones were most desireable.

In order to come to grips with the practical difficulties of focussing the large number of potential abatement programs into a policy-relevant context, the WATAP was applied. The number of potential abatement technologies were further restricted so that the number of potential programs that were examined were reduced substantially. Using WATAP results to determine the least cost set for each smelter, the number of programs in the least cost set was reduced from 54 to 8 in the case of INCO and to 5 in the case of Falconbridge (Ontario /Canada Task Force, Fall 1982:ch. 8).

The analyses revealed that at least one abatement program for INCO, which basically involved installing new smelting technology, would result in a positive return on investment, in present value terms, while reducing emissions. Further SO_2 emission reductions would impose absolute costs on the corporation.

The Task Force commissioned other studies on the financial capabilities and prospects for the two companies, trends and forecasts for nickel and copper markets and the degree to which regional employment and income are dependant on INCO and Falconbridge. This information, together with cost estimates generated during the course of the study, enabled the Task Force to determine the potential economic impacts of specific levels of abatement at the two smelting operations.

The Task Force did not recommend final emission reduction targets for either smelter (Ontario Canada Task Force, Fall 1983:Letter of transmittal). However, in December 1985, the Ontario Government announced a major program called **Countdown Acid Rain** (Ontario Ministry of the Environment, c.1985) which established a schedule of emission reduction objectives for the major SO_2 emitters in the Province, including INCO and Falconbridge. The information developed by the Task Force was undoubtely useful in the development of emission objectives and timetables for the Countdown program. INCO officials also appear to have revised their own estimates of the costs of achieving the relevant SO_2 objectives in light of the Task Force findings.

The Countdown program also requires periodic reporting by the relevant firms on progress being made toward the abatement objectives, including revised cost estimates of abatement projects to be initiated. Just as monitoring emissions and ambient environmental quality is necessary to judge progress on meeting goals, so too the monitoring of past and future costs of these actions is becoming an increasingly important aspect of program management and evaluation.

4.2. Acid Deposition Screening Model

A basic problem in developing a stragegy to reduce acidic deposition is to determine how much emission reduction overall should be achieved and how much each individual source should reduce its own emissions within this context.

Formulating and evaluating strategies for reducing acidic deposition can be an arduous task because of the large number of precursor pollutant emitters and the numerous approaches and criteria that can be used to allocate possible emission reductions among relevant emitters. For this reason, abatement strategy development was critically in need of a procedure to identify and "screen out" the most desireable options from the hundreds of potential configurations of abatement within the relevant geographical region. To this end, an analytical procedure was developed which reduced the number of possible policy options by identifying those strategies which are both efficient in terms of minimizing overall SO_2 control costs and effective in terms of achieving the desired deposition objectives.

A linear-programming based Screening Model was developed for the Ministry of the Environment (Edward A. McBean & Associates, September 1983). The procedure utilizes data from 235 large point-source SO_2 emitters as well as so-called "area" sources and "background" deposition to calculate the change in acidic deposition at 20 specific "receptor areas" that results from specific abatement configurations. For each of the 235 emission sources, SO_2 emission levels are specified along with estimated removal efficiencies and costs of control technologies. Total costs for a technology were calculated as the sum of capital costs and the present value of annual O&M costs incurred over a 20-year period. Prior to being utilized in the linear programming procedure, a sub-model caculated a least-cost abatement function for each major source (Edward A. McBean & Associates Ltd., October 1983). Figure 2 shows a plot of the cost-removal combinations and the least-cost abatement curve for a Canadian power plant.

Screening Model runs produced estimates of the total annualized costs of abatement for given strategies or configurations. The linear programming procedure could determine the least cost configuration of abatement to achieve specific deposition loading targets, or lower, at each of the receptor areas in eastern North America. These results are discussed in Edward A. McBean & Associates (September 1983) and Castel and Griffith (forthcoming).

The results of the Screening Model were presented to various interprovincial and intergovernmental committees and work groups, including Ministers of the Environment, in the course of developing provincial and Canadian positions on abatement objectives for acid rain.

After reviewing the results of the Screening Model, provincial Ministers of the Environment endorsed the principle of achieving deposition objectives in the most cost-effective manner. This principle implied that some provinces, particularly Ontario, would have to undertake a disproportionate share of the abatement effort because its sources tended to be nearest some of the most sensitive receptors. The Screening Model also clearly indicated that abatement in the US would be necessary to achieve the target deposition levels of 20 kg. per hectare-year in all receptor areas.

4.3. Evaluation of Economic Incentive Policies

An aggregate abatement cost function was derived by Peat, Marwick and Partners (July, 1983) for SO_2 emitters in Ontario. This cost function was generated to help evaluate existing and proposed policy instruments that are intended to induce firms to implement required abatement programs. The policies examined include the existing Command and Control regulation and enforcement system augmented by **surety deposits** and **non-compliance (delay) penalties**, **Effluent charges**, and **Transferrable emission rights schemes**.

The analysis incorporated the major industrial emitters of SO_2 in Ontario. Because the three fossil fuel power plants are under common ownership/management (Ontario Hydro), these sources were "bubbled" and analytically treated as a single emitter. Similarly, the 8 petroleum refineries were combined as a single "bubbled" emitter because their total emissions are relatively small and the abatement technologies that could be applied in each plant were identical. Using a computer program, the authors calculated the least cost combination of "strategies" (eg. combination of technologies) that would achieve successively lower levels of SO_2 emissions for the 3 combined power plants and the 8 combined refineries.

Using relevant cost and abatement efficiency data, total cost functions for each emitter were derived. These emitter-specific cost curves were step functions which implies that costs are constant over the emission reduction range of a particular abatement strategy. Cost functions for each of the five "emitters" are summarized in Table 1. Costs are expressed in total annual **private** and **social costs**. Private costs refer to after-tax costs incurred by an individual emitter. Social costs, in the context of the present study, are before-tax costs which reflect the total costs to society of the abatement program regardless of who incurs the costs.

The same algorithm used to "bubble" the power plants and refineries was then employed to determine least cost combinations of strategies that are listed in Table 1 and to construct the aggragate abatement cost curve shown in Figure 3. Annualized social costs (eg. before-tax costs) are plotted on the vertical axis. Each point on this curve indicates a specific combination of emitters and their relevant technologies or strategies. "Tonnes of SO_2 reduced" are plotted on the vertical axis. The origin of the graph (0 tonnes abated) represents the total base (1980) emission level or 1,530,000 tonnes per year.

This minimum aggregate cost of abatement curve is then used to determine the excess cost of not implementing a least cost combination of emitters and abatement technologies. An aggregate abatement cost function is meaningful in this context because acidic depostion is the chief concern. Sulphur dioxide emissions are thus perfectly mixed in the atmosphere before they are deposited as acid rain.

Four command and control scenarios were assessed first. These included pro-rata reductions or cutbacks of 18%, 50%, 67% and 75%. Each of these regulatory scenarios resulted in excess annualized costs ranging from $120 to $400 million (Peat, Marwick and Partners, July 1983:Exhibit VI-1). For example, in order to achieve a 67% pro-rata reduction, emitters would be required by their available abatement technologies (Table 1) to reduce their emissions by 1,238,000 tonnes per year rather than the necessary 1,021,000 tonnes per year. The total costs to achieve this level of abatement would amount to $818 million per year. However, if reductions were orchestrated so as to minimize total costs, the total cost that would result is read from the cost function in Figure 3 as $418 million per year. The pro-rata cutback approach would, therefore, impose an extra $400 million cost on society that is theoretically excessive.

Under an emission charge scheme, a charge rate of $954/tonne of SO_2 would have to be levied to induce emitters to implement abatement sufficient to achieve a 67% reduction in emissions (Peat, Marwick and Partners, July 1983:Exhibit VI-2). A charge would induce this abatement because each emitter would have to pay more in total charges on reduced emissions without abatement than the total of abatement costs plus charges on reduced emissions after abatement. The total before-tax abatement costs incurred would amount to $496 million per year; only $78 million in excess costs rather than $400 million.

Emitters would have to bear private (after-tax) costs of $317 million for abatement plus $413 million in emission charges for a total of $730 million per year (Peat, Marwick and Partners, July 1983:Exhibit VI-3). The $730 million in private cost is higher than the estimated $537 million that emitters would have to bear under the pro-rata cutbacks. However, $730 million is lower than the $818 million that would otherwise be imposed on society.

There is a distributional difference in the two policies as well. Under the pro-rata cutbacks, all of the costs of abatement would be directed to suppliers and installers of the relevant pollution control equipment. Under the emission charge scheme, only $496 million would be spent of the purchase and installation of abatement facilities. The remainder, $413 million, would constitute transfers to government coffers.

Similar analyses were presented for the transferrable emission rights scheme. However, the authors note that, because of the small number of emitters involved, a competitive market for emissions rights is not assured. Moreover, to the extent that the abatement cost functions used in the analyses reflect reality, market participants would likely be willing to buy or sell rights only in "chunks". This could impose a barrier to the implementation of this policy because there could be a mismatch of buyers' requirements and sellers' offerings in terms of both price and quantities (Peat Markwick and Partners, July 1983:VI-12).

These and other analyses of economic based policy instruments have not resulted in any major changes in provincial or federal government regulatory approaches with respect to the environment. The only recent innovation of which the present authors are aware and to which the Peat,2 Marwick study made some contribution is a proposed amendment to the Ontario Environmental statutes. This amendment would give the Ministry of the Environment the discretionary authority to require that a polluter deposit financial security at the outset of an abatement program. This security, which could be in the form of cash, a letter of credit, a surety bond or other negotiable securities, would be returned when required abatement systems are installed. The security deposit would, however, be at risk of forfeiture if agreed-to deadlines were missed. In this way, the deposit would provide a financial incentive to complete abatement programs on time which is otherwise absent with respect to existing enforcement instruments. At this writing (fall 1986), the amendment was in the process of final drafting and review prior to introducion to the Provincial legislature.

4.4. WATAP Assessment of Lime Plants

Air quality studies by the Ministry of the Environment in 1981-2 found that particulate emissions from three limestone quarry and manufacturing operations in Southwestern Ontario caused exceedances of point-of-impingement criteria specified in Regulation 308 of the Ontario Environmental Protection Act. Ministry abatement orders (eg. control orders) were developed to indicate to the plants how much abatement would be required and on which particular outlets in the plants. In the course of developing these control orders, a comprehensive evaluation of the various control options was carried out using the WATAP.

Relevant data on particulate emissions from each outlet in the plants, abatement technologies and their compatibilities, abatement efficiencies and costs and installation times for abatement techologies were assembled. A nominal discount rate of 15% was used in calculating the emission charge scheme, only $496 million would be spent of the purchase and installation of abatement facilities. The rest, $413 million, would constitute transfers to government coffers.

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Relevant data on particulate emissions from each outlet in the plants, abatement technologies and their compatibilities, abatement efficiencies and costs and installation times for abatement techologies were assembled. A nominal discount rate of 15% was used in calculating terms. However, in order to increase abatement from 68% removal to 68.5% removal, costs would almost triple.

Clearly, the Plan which achieves the 61% reduction in particulates is the start of the range of rising marginal costs. One would expect that the firm in question would begin to protest if the Ministry required that particulates be reduced by more than 61%.

The Plan which would achieve the maximum reduction of 68.5% can be interpreted as the Best Available Technology (BAT) since the technologies included are available and they achieve the maximum emission reduction possible short of closing the plant. There is little doubt, however, as to the reaction of the firm if BAT was required in this instance. It is not apparent how one might define Best Practicable Technology in the context of these cost functions since all of the technologies and Plans are considered to be "practicable." As noted earlier in the paper, additional information would be needed to determine the specific abatement objective.

Several other decision criteria can be specified to set emission objectives, including fairness, balancing benefits with costs or achieving ground level concentration criteria for particulates (Regulation 308) at least cost.

Quantitative information on the benefits of specific levels of abatement are not generally available. Fairness can be defined in many different ways. For example, requirements can be specified to achieve equal final emissions at each plant, equal abatement expenditures at each plant, an equal absolute reduction in emissions at each plant or an equal percentage reduction in emission at each plant.

A comparison of the equal percent reduction is indicated on Figures 4, 5 and 6. First of all, a 50% reduction in emission would be impossible for plant B to achieve although it would cost plant A about $700,000 and plant C about $1.6 million to do so, in present value terms. An equal expenditure of, say, $1 million each would yield a 61% particulate reduction by plant A, 22.5% reduction by plant B and a 37% reduction by plant C. Actually, plant C would only have to spend about $600,000 to reduce emissions by 37% or it would have to spend $1.5 million to achieve a 40% reduction.

At this writing, dispersion modelling had not been completed which would indicate which level of emissions would be required for each plant to meet the point-of-impingement particulate concentration guidelines. If such calculations are based on individual plants, the plant-specific cost functions can be used to determine which Plan would achieve the required emission levels at least cost. If perfect mixing of the particulates is assumed, then an aggregate least cost function can be constructed from the WATAP results and least cost combinations of plants and Plans can be determined.

Once an abatement or emission reduction objective is decided upon, the cost estimates of the least cost Plan can be used to assess the economic impacts of the Plan on the firm or establishment.

The information presented in the abatement cost functions and which were used in generating these graphs have obvious uses and advantages to agency personnel during the negotiation for abatement programs. This particular exercise also had a potential benefit to the firms involved. In its submissions to the Ministry, plant B specified its prefered program. The WATAP results indicated that other Plans could be implemented which would achieve the same particulate reductions for the less money or, for the amount of money that the company was willing to spend, Plans were identified which would achieve a greater degree of abatement. These insights were incorporated into the control orders that were finally issued to the plants.

5. Conclusions and Future Work

The work presented in this paper has focussed on cost functions for individual establishments using engineering estimates of the relevant technologies and their costs. Little effort has been made to assemble actual abatement cost data to verify cost estimates or to generate statistical abatement costs functions. Clearly, studies of this nature could yield some very interesting and potentially useful results. Such studies could also improve the accuracy of the cost estimates generated by tools like the WATAP.

However, in many pollution control and regulatory situations, a high degree of accuracy is not critical. We need only get an idea of the range of gradually rising costs as were illustrated in the lime plant example and the approximate location of any discontinuities or large increases in cost for a small gain in abatement to help in designing control programs. Cost information can also be used in negotiations with firms who claim that the cost of compliance will be excessive and damaging to them.

These analyses are, however, data intensive and time consuming. They should not be applied accross the board in an uncritical manner. However, for major initiatives such as the Municipal-Industrial Strategy for Abatement (MISA) or the Great Lakes Remedial Action Plans, the systematic derivation of relevant cost functions and their use in evaluations and assessments can help ensure that these programs are implemented in manner that is fair, efficient and, perhaps most important of all, effective in acheiving the program goals.

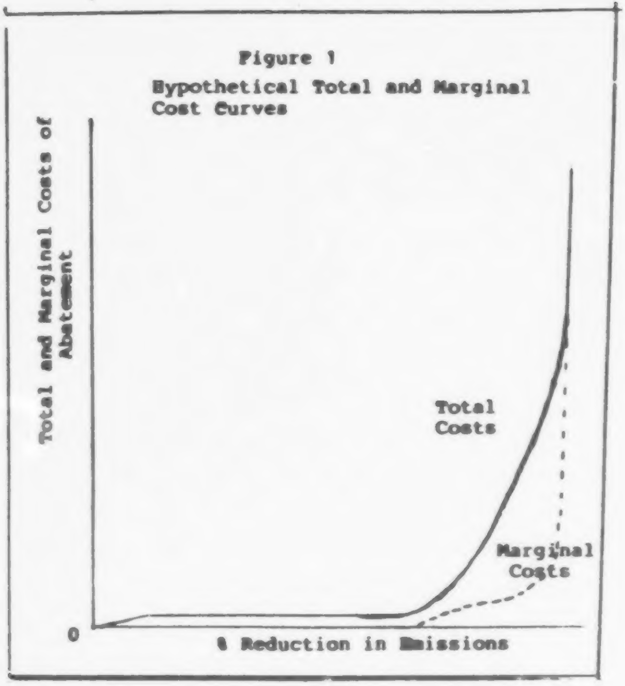

Figure 1

Hypothetical Total and Marginal Cost Curves

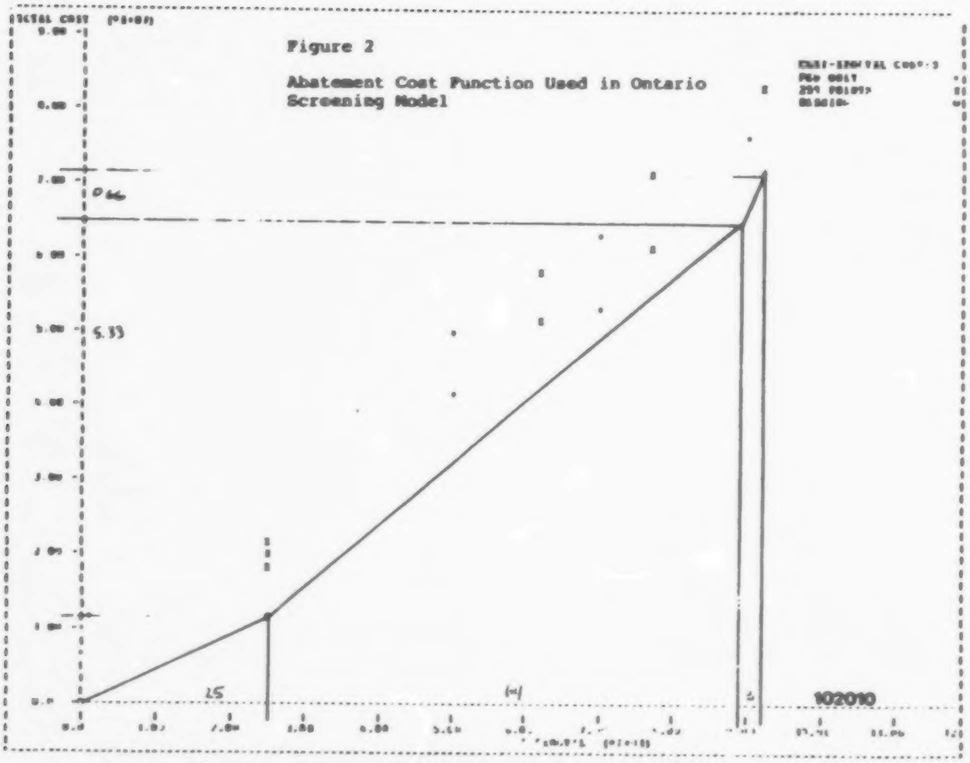

Figure 2

Abatement Cost Function Used in Ontario Screening Model

Source: Edward A. McBean and Associates Ltd (October 1983)

Table 1

SUMMARY OF ABATEMENT STRATEGIES AND ASSOCIATED COSTS
(INCLUDING BUBBLES)

SOURCE	ANNUAL BASE EMISSIONS (000 TONNES)	ABATEMENT STRATEGY[1]	ABATEMENT (000 TONNES)	REMAINING EMISSIONS (000 TONNES)	TOTAL ANNUAL COSTS ($000,000 1982) PRIVATE[2] TOTAL $	PRIVATE[2] $/TONNE ABATED[4]	SOCIAL[3] TOTAL $
Inco	812	0	0	812	0	-	0
		1	306	506	20	65	48
		2	629	183	61	97	151
Ontario Hydro (Bubble)	377	0	0	377	0	-	0
		1	85	292	81	953	96
		2	159	218	153	962	177
		3	240	137	229	934[5]	286
		4	339	38	390	1150	486
Algoma (Wawa)	143	0	0	143	0	-	0
		1	61	82	12	197	26
		2	122	21	21	172	46
Falconbridge	122	0	0	122	0	-	0
		1	107	15	6	56	15
Refineries (Bubble)	77	0	0	77	0	-	0
		1	15	62	15	1000	29
		2	29	48	30	1034	59
		3	41	36	59	1439	120

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1. As noted in the text, a ZERO or no abatement strategy (represented by 0) is included for each source. This is necessary in the analytical work when considering aggregate abatement strategies over all emitters, in which some emitters do not reduce emissions.

2. "Private" costs refer to after-tax costs incurred by individual emitters.

3. "Social" costs refer to before-tax costs and reflect the total costs to society regardless of their incidence, or distribution.

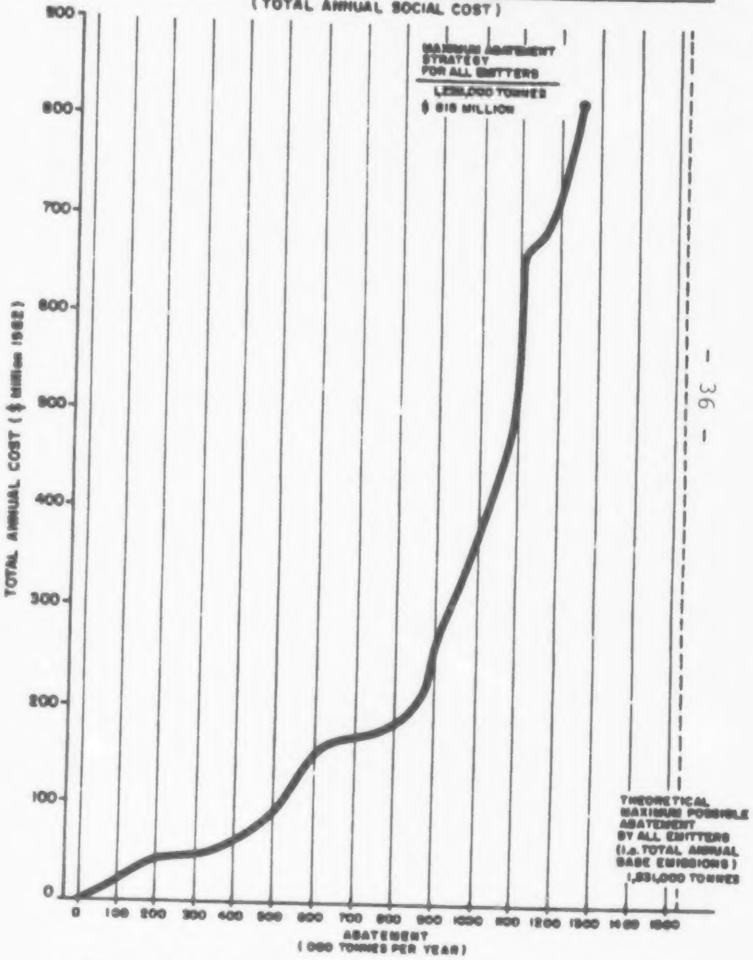
4. We have not included the pulp and paper mills for analysis in this report. On the basis of data from the Ministry, the annual cost per tonne abated is approximately $500 to $600 on a private cost basis.

5. Within the accuracy of the cost data provided, strategies 1, 2 and 3 for Hydro could be considered the same in terms of average cost per tonne abated.

Source: Peat, Marwick and Partners (July, 1983: Exhibit V-4)

Figure 3

MINIMUM COST OF ABATEMENT CURVE FOR ALL EMITTERS AS A GROUP



Source: Peat, Marwick and Partners (July, 1983) Exhibit V-5

NOTE

FIGURES 4, 5 and 6 WERE UNAVAILABLE AT TIME OF PRINTING

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Measuring Social Costs of Electrical Exports and Cost Recovery Opportunities of Environmental Pollution Control at Ontario Hydro

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1.0 INTRODUCTION

Electrical energy production from fossil-fuel generation provides significant benefits to the people of Ontario which are tempered somewhat by impacts to the environment. These potential impacts to society are, in turn, partially compensated by the re-cycling and re-use of environmental byproducts created during combustion. This paper will review the social costs resulting from fossil generation used to provide export to the United States and will also list the value of re-usable products resulting from environmental controls and which bring a benefit to Ontario Hydro customers.

The National Energy Board of Canada require us to provide evidence, in our application for electrical export license, that the price charged would recover an appropriate share of all costs, including social costs, incurred in Canada. These social costs, resulting from emissions due to fossil-fired electrical export sales to the United States, are a cost component of Ontario Hydro pricing agreement. In 1986, this social cost value is established at 0.04 cents/kilowatt hour or one to two percent of the overall price. This report will outline procedures for assessing potential environmental impacts and calculating social costs.

In addition to this cost recovery, Hydro also has policies concerning the sale of by-products of their operations. Presently markets have been found for the sales of ash from fossil-fired stations, cobalt 60 from nuclear reactors, timber from right-of-ways and waste oils from all facilities. Markets are being sought for tritium, deuterium and waste heat sales. These private benefits will be highlighted in the latter part of the report.

2.0 SOCIAL COSTS OF ELECTRICAL EXPORTS

Before granting an electricity export license, the NEB must satisfy itself, at a public hearing, that the price to be charged is "in the public interest." Part of the evidence submitted by Hydro in this regard relates to recovery of the appropriate share of the costs incurred in Canada, including social costs. At one such hearing in 1973, Ontario Hydro argued that there were no social costs since its submissions were meeting the regulation for "point of impingement concentrations" in accordance with the 1971 Ontario Environmental Protection Act. Further, Ontario Hydro contended that Ontario Regulations were consistent with the objectives of the Federal Clean Air Act. Intervenores suggested that the social costs were measurably large and that Ontario Hydro export energy sales were not recovering these high social costs.

The NEB approved a two-year export license which strongly recommended that for the next set of hearings in 1976, Hydro should prepare and present results of social cost studies.

In 1974, Hydro commissioned external consultants to carry out literature surveys to assess potential environmental impacts and damage costs in six areas: health, buildings, clothing, Great Lakes affects, vegetation and animals and property values.

Table 1 briefly outlines the results of the studies and the social cost estimate.

These series of consultant reports were the first useful contribution to the understanding of the social effects of atmospheric emissions in which damage estimates were to be recovered. As a result, for the purpose of pricing export energy from fossil-fired sources in Ontario [Lakeview and Nanticoke Thermal Generating Stations (TGS)], the social cost of emissions in Canada was estimated at between 0 and 0.31 cents/kilowatt hours (1986$).(1) The mid-point of this range was established as the actual pricing value.

In 1979, Ontario Hydro again applied to the NEB for an export license. The same six receptor categories were reviewed by external consultants except the Great Lakes effects were expanded to include impacts on inland lake water quality. They came up with little that was new in the area of effects. However, they did find that between 2 and 4.2 percent of the total acid deposition in Ontario lakes could be related to emissions from Hydro's TGS. The social cost component was estimated at between 0 - 0.05 cents/kilowatt hour (1986).(2) This range was less than the 1974 value by a factor of ten, due to new research information and improved calculation methodologies. Different from 1974, the maximum value was used for pricing.

In 1982, Ontario Hydro, Production Branch, formed a Social Cost Steering Committee to oversee all future studies. In 1984, this

Committee decided to update the consultant studies, this time using internal resources only. Only five areas were reviewed:

1. Health effects.
2. Aquatic ecological systems.
3. Terrestrial ecological systems.
4. Building materials.
5. Property values.

Hydro's export license is valid until 1991. However, Hydro does review these social costs periodically and if necessary revise the social cost value. This most recent reassessment of the literature and calculated social cost is reviewed in detail below.

2.1 Results of the 1984 Social Cost Update

The object of the 1984 review was to update the 1980 consultant report on the effects and social costs of air pollution produced or influenced by fossil-fired emission due to export generation. Attention was focused on acid gas emissions levels for 1982 and forecasted for 1986 and 1989.(3) For ease of presentation only calculations to 1986 will be presented. Social costs for other years will vary according to deposition levels and escalation values.

Human Health - Literature Review

The human health literature review(4) covered: epidemiological studies of air pollutants (long-term or irreversible health effects), controlled human studies (short-term effects), and animal studies (biological mechanism of a certain response). Furthermore, human exposures to indoor air pollutants were also assessed.

The main pollutants assessed for health effects were SO_4, SO_2, NO_x, particulates, polynuclear aromatic hydrocarbons (PAH), radionuclides and trace element emissions, total sulphate and nitrate aerosols, and acid deposition. Health effects were extended beyond the "normal" segments of the population to effects on "sensitive" groups such as people with chronic obstructive pulmonary diseases, the very young, the elderly and subjects with reactive airway diseases (eg, asthma).

Also included were the effects of deeper penetration and greater inhaled volumes of air pollutants in exercising subjects.

Current medical and epidemiologic studies indicated that:

- SO_2, by itself, is an atmospheric constituent at present ambient concentrations. However, SO_2 may be associated with mortality at levels much higher than the current US primary standard. The results concerning respiratory effects of SO_2 on asthmatics and people with normal responses at concentrations in the range of 0.1 to 4.0 ppm, are mixed and contradictory.

- The levels of NO_2 in Canada are relatively low and the present standards seem adequate to protect human health.

- There is no direct evidence of adverse effects of sulphate (SO_4) on humans at current US ambient levels - 25 $\mu g/m^3$, an order of magnitude higher than those registered by the Ontario Hydro monitoring network.

- Statistical studies conducted for broad segments of the US urban population (macroepidemiological studies) provided indirect evidence of a weak but potentially significant relationship between air pollutants (SO_4 and TSP) and human health.

- The contributions of radionuclides, trace metals and organics to the atmosphere from fossil-fired generating stations are insignificant.

- Current medical and microepidemiologic literature indicate that acid deposition presents no direct health problems. There is no information on the contribution of acid rain to the changes in concentration of contaminants in drinking water. It appears that acid precipitation has not affected groundwater to a measurable extent in sensitive receptor areas in Ontario.

Human Health - Social Cost

Two independent methods, based on macroepidemiological studies by Lave and Seskin(5) and Freeman(6) were used to estimate health and social costs even though there is no direct evidence to link emissions and increased health costs. The macroepidemiologic literature indicates the potential existence of a weak but statistically significant relationship between air pollutants and human health. Elasticity* estimates, which include the dose/response relationship between air pollutants (SO_4 and TSP) and human health, were used to generate a mortality and morbidity social cost range for Lakeview, Nanticoke and Lambton TGS (within 30 km) and the remainder of Ontario. The calculation formula is outlined in Appendix 1. Table 3 summarizes the overall social costs for 1986.

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*Elasticity - Unit free number that represents the expected percent change in mortality or morbidity rates associated with a doubling of the mean pollution value.

Table 3

Range of Health Social Costs

[Cents/kW.h of fossil exports (1986$)]

Station/Region	Year 1986
Lakeview	0-0.015
Nanticoke	0-0.005
Lambton	0-0.005
Ontario (beyond 30 km of TGS)	0-0.066
Total Range	0-0.090
Most Likely Value	0.031

Aquatic Ecosystems - Literature Review

The aquatic study (7) reviewed the effects of air pollutants, primarily the acid precursors, SO_2 and NO_x, on the aquatic environment: water quality, bacteria and fungi, primary producers, invertebrates, amphibians and fish. Little evidence exits to suggest that photochemical oxidants (ie, ozone), trace organics (eg, PAH's), radionuclides or trace metals resulting from fossil-fired emissions have significant effects on the aquatic environment.

Acidification of lakes can result from long-range transport of acid gases, natural processes such as water table fluctuations, chemical weathering, natural inputs of organic acids and watershed management activities (logging, farming, etc).

Reduction in lake pH and alkalinity and subsequent increases in heavy metals can affect lake decomposition processes, species diversity and composition of aquatic biota. Fish populations are mainly affected by reproduction failure but can also be affected through direct mortality, reduced growth, selected deformities, and heavy metal uptake.

Aquatic Ecosystems - Social Costs

The primary social costs associated with atmospheric deposition in the aquatic environment are related to the sport fishing industry. Commercial and subsistence fisheries as well as other forms of aquatic recreation were neglected since these fisheries were either primarily centred in non-sensitive areas or areas of negligible deposition due to export power, of relatively low economic value or not seen to be affected substantially by acidification.

In calculating losses to the sport fishery the sensitive areas of Ontario receiving deposition from exported power were approximated for the Ontario Ministry of Natural Resources (MNR) regions of Algonquin, Northeastern and Northcentral. Based on alkalinity data published by the Ontario Ministry of Environment(8) the proportion of lakes in each region susceptible to acidification was determined and the time to acidify for those lakes was calculated based on projected deposition data with and without the export of power.(3) Since the hydrogen ion loading rate in the Northcentral Region did not exceed 50 meq/m^2/yr, the level at which lake acidification was assumed to occur, it was assumed that the lakes in this area would not acidify from long-range transport. Fishing expenditure and participation data from Bedi(9) were the basis for calculation of the reduction in expenditures and angler-days in sensitive areas due to exported power.

An amenity value was calculated based on travel costs for loss of participation in sensitive areas. The amenity value represents about half the total social cost value. It does not represent lost expenditure from Ontario, only a shift of expenditure from an acid sensitive lake area to a non-sensitive area within a 50 km distance. Appendix 2 outlines the calculations and Table 4 summarizes the results.

Table 4

Range of Sport Fishing Social Costs

(Cents/KW h of fossil exports 1986$)

Region	Year 1986
Algonquin	0-0.003
Northeastern	0-0.01
Total Range	0-0.013
Most Likely Value	0.007

Terrestrial Ecosystems - Literature Review

The terrestrial report(10) reviewed the effects of SO_2, NO_x, O_3, trace metals and acid precipitation on crops, forest production, vegetation and animals. Air pollution effects on crop yields have not been adequately quantified although they would vary (positively or negatively) according to species, pollution type and concentration and duration of exposure. Experimentally derived dose-response relationships have been estimated for mainly O_3 and SO_2. TGSs do not emit ozone but may influence its concentration through atmospheric chemical processes.(11)

Although some tree species are sensitive to SO_2 and O_3 under controlled experiments, to date ambient SO_2 and O_3 concentrations in Canada have not been demonstrated to cause reduced forest productivity. Laboratory and controlled field experiments using simulated acid rain have produced positive and negative results. The nitrogen and sulphur, which are essential elements for tree growth, have a fertilizing effect and can stimulate growth of tree seedlings used in experiments.

Tree growth decline and die-back observed in West Germany and the Northeastern US may involve a complexity of causes, more than just acid deposition, such as drought, SO_2, O_3, insects, pests and trace metals.

The indirect effects of air pollutants on animals through habitat modification (reduction in food, loss of habitat, etc) are probably greater than direct effects (trace element ingestion, reproductive problems, etc). Field studies conducted to date indicate that animals may avoid areas of higher pollutants or adapt genetically.

Terrestrial Ecosystems - Social Costs

No social costs for the effects of air pollutants from fossil-fired stations can be calculated for reductions in crop yields or forest productivity. However, although dose-response relationships and estimates of the value of crop loss due to O_3 have been reported, a determination of Ontario Hydro's export emission contribution to O_3 production in sensitive receptor areas is required before any social cost values can be calculated.

For animals, the methodology from the above mentioned aquatic report(7) was broadened to determine the social cost on aquatic based wildlife (waterfowl, otters and muskrats) (Table 5, Appendix 3). The loss of the aquatic food base through lake acidification would result in a reduction in hunting and trapping activities (recreation days). Only participation of resident hunters in the affected regions of Ontario were used to calculate an amenity value and its subsequent loss with reduced waterfowl hunting opportunities.

Table 5

Range of Hunting and Trapping Social Cost

[Cents/kW.h of fossil exports (1986$)]

Region	Year 1986
Algonquin	0-0.001
Northeastern	0
Total Range	0-0.001
Most Likely Value	0

Structural Materials - Literature Review

Damage to economically significant structural materials (ie, concrete, metals, building stone, paints, textiles and glass), from SO_2, NO_x, particulate matter and acid rain was reviewed.(12)

The susceptibility of a material to damage is related to:

- Reactivity of the material to acidity.

- Moisture, acid gases and/or particulates on material surface, (exposure is a function of location and ambient pollution levels).

- Physical forces resulting from the volume changes associated with changes in the chemical composition of the material.

Damage to structural materials including historical property can be in the form of corrosion of metals, decay of building stone, erosion and colouration of paints and the weakening and fading of textiles. All of these effects occur to a significant degree as a result of, or in association with, natural environmental conditions, eg, moisture, O_2, CO_2, sunlight, particulate matter, etc. Quantification of the specific contribution of each factor, nature or anthropogenic, to materials' deterioration is difficult.

Structural Materials - Social Costs

The method of calculation of the social costs of fossil-fired emissions on structural materials was based on the Acres (1980)(13) and Salmon (1970)(14) methods with some modifications derived from the MOE (1984).(15) (Appendix 4).

Damage to the following structural materials was estimated: concrete, zinc, copper, aluminum, nickel, tin, paint, brick, stone and glass. Only damage costs due to dry deposition of SO_2 and wet deposition of SO_2 + SO_4 within Ontario were considered (Table 6). Soiling costs and a value of damage to cultural/historic property were not estimated because of a lack of reliable information. In the Acres (1980) report(13) the soiling costs for Lakeview, Lambton and Nanticoke TGS amounted to about 5% of the total soiling and deterioration costs combined (no estimate for cultural property effects was given).

Table 6

Range of Structural Material Social Costs

[Cents/kW.h of fossil exports (1986$)]

Region/Station	Year 1986
Northern Ontario	0
Southern Ontario	0.001-0.004
Lakeview	0.001-0.002
Nanticoke	0
Lambton	0.001-0.002
Total Range	0.003-0.008
Most Likely Value	0.005

Property Values - Literature Review

The results of 18 empirical urban studies were compared.(16) While almost all found a significant effect on property values, all were conducted under conditions of high pollution of the 1960's and 1970's mainly in US cities. The applicability of the results to the significantly low population levels in urban Ontario 20 years later is questionable.

Given the generally low pollution levels, the lack of variation in air quality within cities and the marginal contribution due to Ontario Hydro exports, air pollution due to exports is unlikely to be perceived by urban homeowners. Therefore, there is no likely social cost estimate for Ontario urban property.

Potential approaches to measure the effect of acid precipitation on rural property values were compared and evaluated. The market or implicit price model was found to be most applicable. The proposed model was described for potential application to recreational properties possibly in the Muskoka-Haliburton area. Data requirements, sources and availability were reviewed. It was concluded however, that because of the high cost and lack of apparent effects at the present time, it would be premature to conduct the empirical research.

3.0 REVENUE FROM ENVIRONMENTAL POLLUTION CONTROLS

As a result of Ontario Hydro's operations a number of by-products are formed. Attempts are made to recover revenue from them instead of directly discharging them to the environment. Since 1980 revenue has been generated from the sale of ash from fossil-fired stations, cobalt 60 from nuclear stations, timber from right-of-ways and waste oils from many locations throughout the Corporation. Future markets are being pursued for the sale of tritium, deuterium and heat energy.

Ash

Ontario Hydro successfully markets coal ash from TGS. In doing so not only is revenue generated but expenditures are saved on disposal costs. Over the last several years ash sales have been expanded into cement manufacturing processes and concrete applications and more recently into the clay brick, and, as stabilizing material for waste treatment industries. The historic use of ash in land reclamation projects and as structural fills in highway development has been maintained.

The past 5 years sales of these materials is shown in Table 7.

Table 7

Revenue and Disposal Savings of Coal Ash from TGS 1981-1985

Item	1981	1982	1983	1984	1985
Coal Ash Quantity (Mg)	157 870	99 000	138 648	190 440	211 178
Value of Sales ($)	146,990	67,742	126,687	207,878	296,295
Disposal Savings ($)	441,098	169,360	309,596	391,186	476,693
Total Benefits ($)	588,088	237,102	436,283	599,064	772,988

Timber

In the initial clearing of right-of-ways the original land owner has the right to purchase the timber cut at Hydro's cost. If he relinquishes this option, Hydro then calls for public tenders. In most cases Hydro only recovers its costs and therefore no revenue is generated.

Isotope Sales

For many years, Hydro has been selling isotopes unique to the CANDU nuclear system around the world.

Cobalt 60 remains the most important isotope. Under arrangement with Atomic Energy of Canada Limited (AECL) Hydro produces about 85 percent of the world's supply for marketing by AECL (Table 10). It is used in cancer therapy, for sterilizing hospital supplies and for the preservation of food. Over the last five years revenue in the order of 5 M$ to 10 M$ per year has been generated.

In the coming years markets are expected for deuterium gas (fibre optics), deuterated lubricants (long-life oils), and tritium (runway markers for remote airstrips).

Table 8

Quantities of Cobalt 60 Sold from Nuclear Stations 1981-1985

Item	1981	1982	1983	1984	1985
Cobalt 60 Quantities (Mg)	12.36	13.07	11.3	8.63	21.33

Waste Oil

In Southern Ontario waste oil is shipped to Ontario Hydro's Kipling St. Complex where it is stored in a tank form for bulk sales to reprocessors. In Northern Ontario batch holdings of waste oils are sold to local reprocessors from individual Hydro sites (Table 9).

Table 9

Sales of Waste Oils from Hydro Facilities

Item	1981	1982	1983	1984	1985
Reclaimed Oil Sales (Gallons)	70 000	70 000	70 000	70 000	70 000
Value of Sales ($)	100,000	110,000	110,000	95,000	70,000

Heat Energy

Hydro is developing markets for the sale of steam and hot water to industries in close proximity to generating stations. This steam will be 65 percent cheaper than steam generated by conventional sources.

The largest of these developments is the Bruce Energy Centre adjacent to the Bruce Nuclear Power Development. It will be ready for occupancy by the fall of 1986. Chemical, food processing, fibre board, plastic molding companies and greenhouse manufacturers are the main industries interested in waste heat.

Ontario's first commercial fish farm, Coolwater Farms, will utilize warm water discharge from Pickering Nuclear Station in 1986 to accelerate the growth rate of perch and trout fingerlings.

4.0 SUMMARY

Ontario Hydro recovers social costs from its electrical exports and revenue from by-products of its operations, thus reducing the total cost of energy production to its customers.

Social Costs

Export sales to the United States have benefited Ontario residents over the years by reducing annual rate increases up to seven percent. These export sales which equate to about five percent of our total annual production can have a community and environmental impact. The five social cost studies reviewed the effects of fossil-fired emissions (mainly SO_4, SO_2, NO_x, particulates, trace elements and acid precursors) generated as a result of US exports, on sensitive receptor areas - human health, aquatic and terrestrial ecosystems, structural materials and property values.

There is no direct evidence of long-term epidemiological effects on people attributable to these emissions for exports from Hydro's largest fossil-fired stations Lakeview, Nanticoke and Lambton TGS. However, these emissions can contribute to long-range transport and ultimately contribute to lake acidification in sensitive areas. This in turn can lead to changes in lake community structures.

Air pollution effects on crops and timber yields have not been adequately quantified to be of valid concern. Effects that have been observed cannot be directly related to fossil-fired emissions (ie, ozone effect on crops, biophysical effects on forests).

Lake acidification can have an indirect effect on the aquatic food base for waterfowl and furbearers.

Structural materials are susceptible to damage from dry and wet deposition. Susceptibility is related to material reactivity, moisture levels, surface exposure and pollutant concentrations.

In both urban and rural areas the effects of fossil-fired emissions/deposition on property values is not perceived as an issue. This includes the effects of lake acidification on recreational property.

The following is a summary of the social cost estimates, based on the five separate studies (Table 10).

Table 10

Summary of the Most Likely Values of Social Costs

[Cents/kW.h of fossil exports (1986$)]

Receptor	Year 1986
Human Health	0.031
Aquatic Ecosystem	0.007
Terrestrial Ecosystem	0
Structural Materials	0.005
Property Values	0
Total	0.043

These values should be considered as approximations, limited by the state-of-the-art of social cost methodology and by the estimates of emission/deposition levels.

The values quoted in Table 9 are approximately the same as the 1980 summary results (Table 2) taking into account the inflation rate between 1980 and 1985.

Revenue from By-Products

In addition electrical export social costs, Hydro also recover costs from many of its by-products such as ash sales, isotopes and waste oils. On an annual basis sales can generate revenue in the order of 5 M$ to 11 M$, mainly from the sale of Cobalt 60.

Table 1

1974 External Consultant Assessment of Environmental Effects and Social Costs of Electrical Exports

Receptor Area	Author	Environmental Effects	Social Costs cents/kilowatt-hour (1986$)
Health	Dr. T. Hamilton* Ontario Hydro(17)	1. Concentration levels in Southern Ontario are at or below the threshold for any measurable causation for: (a) decrease in ventilatory function and increase in respiratory tract infection in children. (b) increase in acute respiratory illness in families. (c) increase in adult chronic bronchitis. 2. Air stagnation during cold weather can aggravate asthmatic reactions in children, elderly and emphasematous.	0-0.14
Building Materials	Acres Consulting(18) Service	1. Some deterioration of material. In descending order of costs: Zinc, Paint, Copper, Nickel, Concrete, Aluminum, Brick, Tin, Stone and Glass. 2. Additional soiling of homes.	0.007-0.17
Textile Products	Ontario Research Foundation (19)	1. No deterioration of textiles. 2. Some soiling by particulates.	0
Great Lakes Water Quality	Acres Consulting Service (20)	Due to the strong buffering capacity of the Great Lakes, SO_2 has no effect on pH, water quality or toxicity.	0

*No external consultant could be found to complete study.

Receptor Area	Author	Environmental Effects	Social Costs cents/kilowatt-hour (1986$)
Vegetation and Animals	F.F. Slaney (21)	No damage to vegetation or health of animals.	0
Property Value	Peat Marwick (22) and Partners	No relationship between air pollution levels and property values in Metropolitan Toronto.	0
		Range	0-0.31

Table 2

1980 External Consultant Assessment of Environmental Effects and Social Costs of Electrical Exports

Receptor Area	Author	Environmental Effects	Social Costs cents/kilowatt-hour (1986$)
Health	Queen's University(23)	1. Normal low ambient pollutant concentrations aggravated with such harmful activities as cigarette smoking makes it impossible to accurately assess chronic exposure effects. 2. Oxides of sulphur and particulates are still the important pollution constituents mainly in children and adults with pre-existing chronic respiratory or cardiac diseases.	0-0.04
Building Materials	Acres Consulting Services(13)	1. Same ten materials as in 1974 were assessed (Table 1) Zinc, paint and concrete accounted for 80% of the total deterioration costs. 2. Acid precipitation can promote corrosion but can also wash away pollutants.	0-0.007
Textile Products	Ontario Research Foundation(24)	Fabric soiling by particulates still the only effect.	0
Water Quality*	Acres Consulting Services(25)	1. Hydro contributes to the loadings of sulphates and nitrates in the Haliburton-Muskoka area (2% - 4%) 2. Hydro emissions would take 23 years to seriously affect sport fishing instead of 24 years without Hydro emission.	0-0.006

*Mainly inland waters

Receptor Area	Author	Environmental Effects	Social Costs cents/kilowatt-hour (1986$)
Vegetation and Animals	Acres Consulting Service(26)	1. No measurable or visual damage to forests due to acid precipitation. 2. Trace element emissions are 1 to 3 order of magnitude lower than ambient criteria and have no toxic effects on animals.	0
Property Values	Peat Marwick and Partners(27)	1. Decline in pollution levels between 1968 and 1978 did not effect urban property prices. 2. No known effects of acid precipitation on recreational or non-urban property.	
		Range	0-0.05

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Appendices

Appendix 1

Format for Calculating the Social Costs of Health Effects

The estimate of social costs for Ontario due to fossil-fired electrical exports is calculated by:

(1) Ontario Health Costs:

total Ontario medical costs (direct and indirect) as a percentage of Ontario GPP x Ontario GPP ($).

(2) Contribution of exports to ground level concentrations (GLC): emission contribution to GLC x portion of overall energy exported (%).

(3) Percent increase in mortality/morbidity due to increase in pollution:

(2) x elasticity*.

(4) Total health costs due to exports:

(3) x (1).

(5) Health costs per kilowatt hours:

(4) x kilowatt hours.

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*Elasticity - unit free number that represents the expected percent change in mortality or morbidity rates associated with a doubling of the mean pollution value.

Appendix 2

Format for Calculating the Social Costs on the Aquatic Ecosystem

The estimate of social costs for Ontario due to fossil-fired electrical exports is calculated using the following formulas:

1. Rate at which lakes acidify due to atmosphere inputs:

$$Ta_1 = \frac{Alk \times Dm}{Ldh_1} \qquad Ta_2 = \frac{Alk \times Dm}{Ldh_2}$$

where Ta_1 = time to acidify with exports

Ta_2 = time to acidify without exports

Alk = total alkalinity of lake water (mg/m^3)

Dm = mean depth (meters)[a]

Ldh = hydrogen ion loading rate ($mg/m^2/yr$)
(h_1, h_2 as above a_1, a_2)
(total deposition rate - 50 $meq/m^2/yr$[b])

2. Percent of lakes sensitive to acidification:(8)
(200 mg/m^3 was assumed to be the upper alkalinity limit, below which lakes would acidify.)

Algonquin	72%
Northeastern	59%
Northcentral	40%

3. Losses in sport fishing participation or expenditures(9) due to exports:

$$[\tfrac{1}{2}\ E \text{ (or P)} \times K \times t_2] - [\tfrac{1}{2}\ E \text{ (or P)} \times K \times t_1] \text{ (Shaded area in Figure 1)}$$

where E = total annual expenditures (half the total annual expenditures for those partially fishing[c] ($)

P = participation in angler days ($)
K = proportion of lakes susceptible to acidification (%)
t_2 = time to acidify without electrical exports (years)
t_1 = time to acidify with electrical exports (years)

4. The above (3) is divided by the total exports in that year to give a loss per kilowatt hours.

5. An amenity value was calculated based on travel costs for loss of participation in sensitive areas.

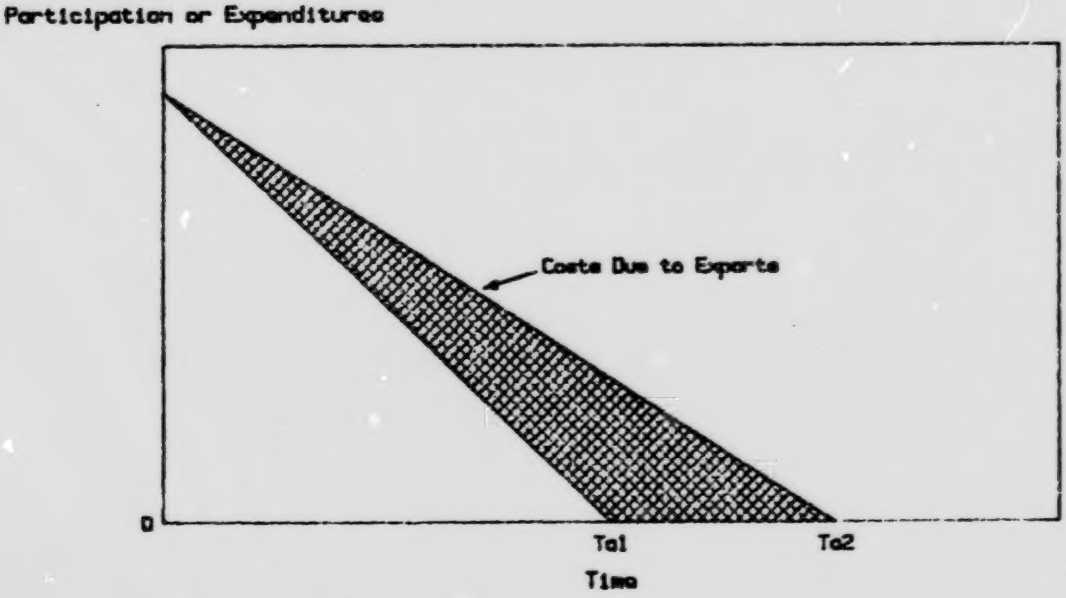
   (a) Minns (1981)(28) estimate the mean depth for 6,205 Ontario lakes is 6.1 meters.

   (b) Dillon et al (1984)(29) suggests that acidification occurs in lakes where deposition is 50 mg/m^2 of strong acid per year or more.

   (c) Expenditures were classed into four categories:

      (i) Ontario residents solely for sport fishing
      (ii) Ontario residents partially for sport fishing
      (iii) Non-residents solely for sport fishing
      (iv) Non-residents partially for sport fishing

FIGURE 1
Representation of the Derivation
of Losses Due to Electrical Exports



Ta1 - Time to Acidify with Exports
Ta2 - Time to Acidify without Exports

Appendix 3

Format for Calculating the Social Costs on the Terrestrial Ecosystem

The estimate of social costs for Ontario due to fossil-fired electrical exports is calculated as follows:

1. Fishing losses through lake acidification, (Appendix 2) is broadened, to the further implications for hunted piscivorous (fish-eating) waterfowl, other waterfowl, otters and muskrats,

   $$(\frac{1}{2} E \text{ (or } P) \times K \times t_2) - (\frac{1}{2} E \text{ (or } P) \times K \times t_1)$$

   where E = total annual expenditures on waterfowl hunting ($)

   P = participation in waterfowl hunter-days ($)

   K = proportion of lakes susceptible to acidification (%)

   t_2 = time of acidify without electrical exports (years)

   t_1 = time to acidify with electrical exports (years)

2. The above (1) is divided by the total exports in that year to give a loss per kilowatt hour.

3. Use formula in (1) and recalculate and add to formula (1) the revenue lost for furbares pelts by substituting revenues from pelts for waterfowl hunting expenditures.

4. An amenity value was calculated based on travel costs for loss of participation in sensitive areas.

Appendix 4

Format for Calculating the Social Cost on Building Materials

The estimate of social costs for Ontario due to electrical exports of fossil-fired emissions is:

$$E = \left(\frac{\Sigma D_r + S + H}{P}\right)$$

where E = estimate of social costs per kilowatt hour due to export of electricity;

ΣD_r = total value of materials damage in region r (eg, sum of value of damage to zinc, concrete, etc, due to corrosion, erosion, etc);

S = soiling costs;

H = value of damage to cultural properties;

P = number of kilowatts of electricity produced by fossil-fired generating stations for export.

The value of material damage is estimated by:

$$D_r = C \times L \times V \times E \times I_r \times P_r$$

where D_r = annual economic value of damage to a specific material in region r;

C = annual consumption volume of materials in Ontario;

L = average economic life of the material;

V = value added or labour factor;

E = exposure factor;

I_r = interaction value in region r;

P_r = population factor for region r.

QUEBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS:

WHAT LESSONS HAVE BEEN LEARNED

Paper presented at the Environmental economics session of
the Technology Transfer Conference
Toronto, December 8, 1986

By: Claude Sauvé, economist

Direction des stratégies et
politiques environnementales

Ministère de l'environnement du Québec

INTRODUCTION

As in other governmental instances, the Government of Quebec introduced, in June of 1981, the requirement to evaluate the economic implications of new regulations that may have an effect on industry. This requirement applies in particular to legislation of a social character and especially to environmental regulations.

The adoption of that measure was made in a general context of deregulation - should we call it the first step of the present deregulation wave - that concentrated on the burden that government regulations impose on the private sector. Governments across North America where becoming more and more conscious that their importance in the economy had grown considerably on the preceding decades and that the costs tied to their different interventions particularly regulations, were bearing more and more heavely on their economic system.

Here in Canada, let us recall that following the First Ministers meeting of February 1978, the Economic Council of Canada had been requested to "undertake a number of studies of specific areas of government regulation which appear to be having a particularly substantial economic impact on the Canadian economy".

Under that "regulation mandate" the Council produced a number of position papers and studies in the following two years which still fuels the deregulation debate. Meanwhile the Federal government had taken the lead by initiating its own Socio-Economic Impact Analysis (S.E.I.A.) by August 1978.

Under the E.C.C. mandate, environmental regulation was clearly identified as one of the areas perceived to impose substantial negative impacts on the economy. Since the mid 1960's, regulatory activity was particularly intense in the environmental sector. As an illustration, let us only consider that there were at least eleven studies on environmental regulations that were commissionned by the Council under its mandate.

In the U.S. it was at the beginning of (1981) that President Ronald Reagan issued a new Executive Order that emphasized the importance a measuring the costs and benefits of federal regulations, stressed the significance of the resulting analysis and put the Office of the Management of the Budget (O.M.B.) in a central role to ensure compliance with the cost/benefit procedures. That Executive Order replaced the Carter administration's own regulatory analysis review program initiated in 1978.

More recently, the debat has widened to the general theme of government intervention in the economy and has become, in Quebec, one of the central theme of governmental policy.

The publication, at the beginning of this summer, of a series of reports on government organization, deregulation and privatization by work-groups appointed by the Quebec government and the privatization of a number of Crown owned enterprises mark clearly the will of the present government not only to engage in an active deregulatory process but also to lessen the importance of government related activity in the economy.

We can immediatly establish a parallel with the Nielson report to the Federal government and realize that the context is evolving in a somewhat systematic fashion.

The Quebec economic evaluation of new regulations procedure

The economic evaluation procedure was introduced by Cabinet decision on June 1981. It required that all proposed regulations submitted to Cabinet be accompanied with a summary of an impact study done by the proposing Ministry. The study summary should be along the general outlines described in table 1.

The procedure was designed to be applicable to all forms of new regulations including modifications to existing regulations.

From an administrative standpoint, in addition to the standard rulemaking and Cabinet approval process, a proposed regulation with its accompanying impact study had to undergo the scrutiny of the Permanent Ministerial Comittee on Economic Development which generally coordinates Ministries actions and advise government on economic development matters.

In fact, the new procedure introduced a new actor in the negociation process that a regulation has to go through before going for Cabinet approval.

TABLE 1

Outline of an Economic evaluation study

A) Description of the problem and major objectives:

1. Advantages and disadvantages of the present situation.
2. Comparison with the situation elsewhere.

B) Possible action scenarios.

C) Description of the options considered.

D) Economic evaluation of the options

1. Benefits
   - User's benefits
   - Benefits accruing to industry
2. Costs
   - Investment costs
   - Production costs
   - Transaction costs
   - Indirect costs

E) Governmental impacts

- Budgetary impacts
- Fiscal impacts
- Coherence with other governmental actions

It should be stressed, as this point, that we have not yet used the term Cost/Benefit Analysis (C.B.A.) to describe the economic evaluation process. Looking at the general outline in table 1, you don't find any explicit reference to it. Not that it is excluded as such, but the general philosophy behind the evaluation is more in terms of introducing an economic rationality in the designing of regulations than the systematic application of a technique.

Another thing we want to stress, and that doesn't comme out clearly in table 1, is the importance given to the formulation of alternatives to regulations in the evaluation process. The basic idea was to introduce at the base of the regulatory process the consideration of complementary or alternative modes of intervention and to evaluate them comparatively to the regulatory approach.

Finally, even if the focus was on economic evaluation, the framework of the impact study was designed to cover systematically the rationale, the formulation of specific objectives and government impacts. These aspects were already covered in the standard "memoires" to Cabinet but not in a technical fashion. In effect "memoires" can be conceived as negociation documents in the regulatory process compared to economic evaluation studies which are more technical in nature.

The economic evaluation process at the Quebec Ministry of Environment

Like all other Environmental Agencies, the Quebec Ministry of Environment relies mainly on regulations to promote its objectives of environmental quality.

"Regulation production" is therefore an important continuing activity at the Ministry. The economic evaluation procedure was then perceived as a threat to those activities, and surely an additional obstacle in the already difficult rule-adoption process.

In addition, putting dollar figures on the environment didn't quite fit the environmental culture inherited from the earlier decades. Consequently, it wont surprize anyone to say that the introduction of the economic evaluation procedure was a difficult process.

Most of the ministries major pieces of regulations having been adopted in the second half of the seventees, the economic evaluation procedure applied essentially to modifications of these. To give a better perspective of the environmental regulation universe in Quebec, let us consider that there are essentially eleven (11) regulations which have a major environmental thrust.

Since 1981, one new regulation was introduced (drinking water) and there has been amendments to at least five existing regulations. Each of these went through the economic evaluation process. We have to add to that, a number of amendments on the majority of the remaining regulations which are still in the Ministries pipeline uncluding a new regulation on pesticides. For all of those, the economic evaluation procedure is applied.

Considered at the beginning as an impedement to the Ministries regulatory action, the evaluations were made at the end of the line of the internal rulemaking process. Collaboration with those responsible for the elaboration of the regulations was difficult: The new procedure was considered, in fact, a loss of power by the rulemakers. Someone had changed the rules of the game. The traditional conflict between economic and environmental values had to be faced and resolved.

Since then, the situation has evolved and the economists responsables for those evaluations are progressively involved in the rule making process. A new dynamic has been created and the results to date indicate we are progressively going from a symbolic approach to a more pragmatic approach in regulatory action.

For those who are not familiar with the symbolic nature of environmental regulations, reference should be made to the numerous studies on environmental regulations made under the E.C.C. regulation mandate and the recent studies commissionned by the Law reform Commission of Canada.

Suffice it to quote, from the Thompson Study made under the regulation mandate

> "... bargainning is the essence of the environmental regulatory process as it is practiced in Canada... the reality is that the rules of environmental regulation are never clearly stated or certain, except in a purely symbolic sinse."[1]

---

[1] Andew R. Thompson, "Environmental regulation in Canada: An Assessment of the Regulatory Process". A study prepared for the Economic Council of Canada by the Westwater Research Center U.B.C., 1980.

Problems and lessons

In doing those economic studies we have encountered a number of problems and learned quite a few lessons.

One of the basic problems we've encountered is the lack of environmental data.

Here, the problem can be broken down into two components. First, the lack of a specific scientific database and expertise creates a situation where in many fields of environmental activity the Ministry has to rely on international or federal data and expertise complemented with factual information. Second, the scientific database is not adapted to provide the kind of input necessary for precise benefit description. Neddless to say that dose-response relationships are a rare species.

That kind of situation undermines continually the process of benefit qualification and evaluation and particularly the definition of specific objectives.

In addition, the formulation of alternative options which the evaluation procedure was suppose to generate did'nt work very well. The general scenario was essentially to present two options: the "status quo" and the solution proposed which was, evidently, an amended regulation or a new one. The evaluation study became rapidly a strategic document for the Ministry and the exercice did'nt produce the results expected, at least in the beginning.

The focus, as far as economic evaluation is concerned, was therefore on costs: Investment costs, operation and maintenance costs, paperwork costs.

The case is classical amongst environmental agencies engaged in economic evaluation of their regulation. The process even implicity questioned the scientific foundation of the regulations because of the lack of scientific data.

At a certain point, the economic evaluation study was even perceived as a way of giving the Ministries promoting economic development, supplementary arguments to kill the proposed regulation.

All this looks quite negative but on a second thought, the situation induced the questionning of the way we were looking at the evaluation and more importantly at regulations.

When we examine the Ministries internal rulemaking process, we find an iterative process in which the economic evaluation study now plays a vital role. In this type of process you can have quite a number of economic evaluation embedded in an evolutionnary formulation of a proposed regulation. In parallel to that we must consider the bargaining process which traditionnaly takes place between the Ministry and other affected government agencies or Ministries and Industry. This last issue has been deal with quite extensively in the litterature, namely Dewees.[2]

The focus being on costs, the first question asked became "Are the costs reasonnable" implying "Can we reasonnably presume that industry can bare those costs?" And we found ourselves doing detailed financial analysis to try to determine if the regulation could have a disruptive effect on industry.

The second question asked was "How does the proposed regulation compare with what you find elsewere particularly in economies were you find competing industries?"

---

[2] Donald N. Dewees, "Evaluation of policies for regulation environmental pollution", Economic Council of Canada by the Westwater Research Center U.B.C., 1980.

That kind of question focusses on what, in the proposed regulation, is different from what they're regulating elsewhere: What is the specific justification for being different?

At this point, it should be noted that this line of reasoning is a long way from comparing the benefits and the costs in the formal framework of Benefit/Cost analysis. The treatment of the costs in such a fashion resulted in considering, at first, technical alternatives to render the costs acceptable to industry whatever the word "acceptable" means without sacrificing any environmental objectives. As far as the benefits are concerned, they are valued for themselves and therefore they are essentially the object of the socio-political system. But the procedure introduced enormous pressures to define and express them in a more articulate manner.

The net effects of this process, in a context of severe budgetary restraint, is twofold. First, a widening of perspective in considering the tools available to reach environmental objectives. Second, increased efforts and resources devoted to the articulation of the benefits of the actions proposed.

The Ministry is in effet quite rapidly moving towards the consideration of complementary alternatives to the traditionnal regulatory approach. It also is engaged in a process of articulating its specific objectives and the benefits derived from its action. Essentially, the Ministry is reacting to its own way of putting the questions of the economic impact of its own regulations.

I would like to conclude, from this breef look at the practical experience of economic evaluation of environmental regulations in Quebec, that:

- The natural reference to the Cost/Benefit Analysis technique when we speak of the application of the economic rationale to environmental problems, may be essentially a problem of terminology with a symbolic character.

The common sense base for the justification of the technique is sound. No one would want to question that. But we must remember that environmental problems still have a high socio-political content in our society. In that sense, benefits are not valued on the same basis as the costs. We just have to look at the acid rain problem to convince ourselves of that reality.

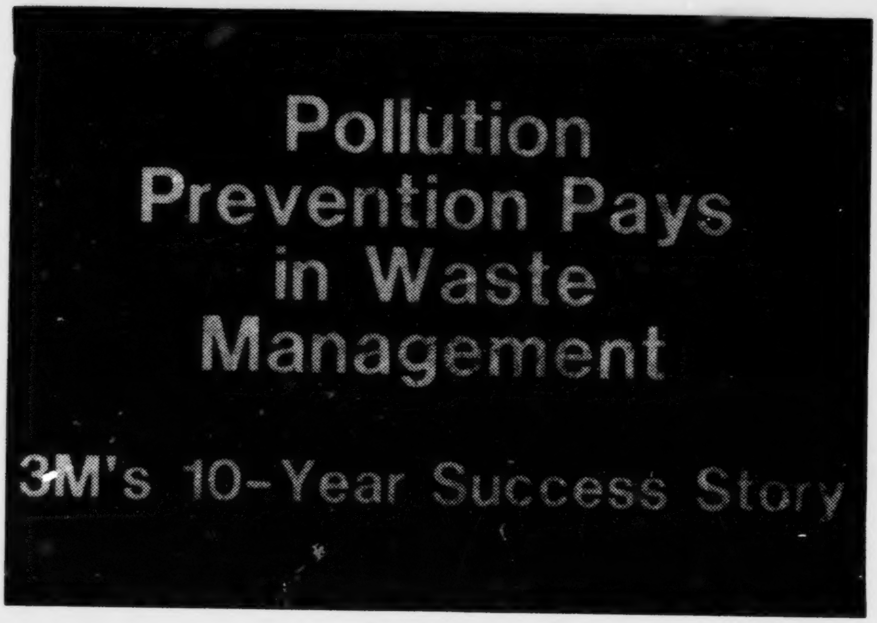
- When we analyse the pattern of change which has taken place at the Quebec Ministry of the environment since 1981, we find that the approach of introducing the economic rationale in the rulemaking process as opposed to the compulsory use of a specific technique like Cost/Benefit Analysis, has had an interesting effect: Scientists and engineers who are intimately involved in the environmental rulemaking process come to view economists and their way of looking at problems, as strategic allies in promoting their environmentals objectives. They are bringing in a new set of tools at a time when the regulatory tool is subject to very strong attacks. We should not confuse what we call "environmental economics" with the application of a technique.

- Looking a our modest experience at the Ministry and at the present worldwide interest in reconcyling economic with environmental principles, I think economists have a point to make: in the present economic context, they have a crucial contribution to make to environmental policy making and this contribution owns more to their attitude and imagination than to their technique.

3M'S POLLUTION PREVENTION PAYS PROGRAM
TECHNOLOGY TRANSFER CONFERENCE - DECEMBER 8, 1986
TORONTO, ONTARIO

Mr. A.G. Mills
Vice-President, Technology Services
3M Canada Inc.

It is indeed a pleasure to participate in this important conference and to describe a program within the 3M Company that has caused a change in the approach that we have taken to developing our products and managing our businesses.



Pollution Prevention Pays in Waste Management

3M's 10-Year Success Story

SLIDE 1

We have had a good deal of publicity over our "Pollution Prevention Pays Program" in the eleven years of its existence. At the outset there was considerable debate as to whether the word "Pays" should be associated with environmental activity. But we identified four valid pay-offs including an improved environment; conserved resources; improved technologies; and reduced costs. Now with over a decade of experience with the Program, we can demonstrate that the Pollution Prevention Pays or that our "3P" concept really does work.

I would like to tell you how the concept evolved, give you some examples of successful projects, and indicate our progress towards "Institutionalizing" the Program and the notion that Pollution Prevention Pays. We feel we will truly be successful when our scientists, our engineers, and technicians keep this notion on their minds as they develop new products and processes.

As many of you may know, 3M is a large multinational corporation with a highly diverse product line.

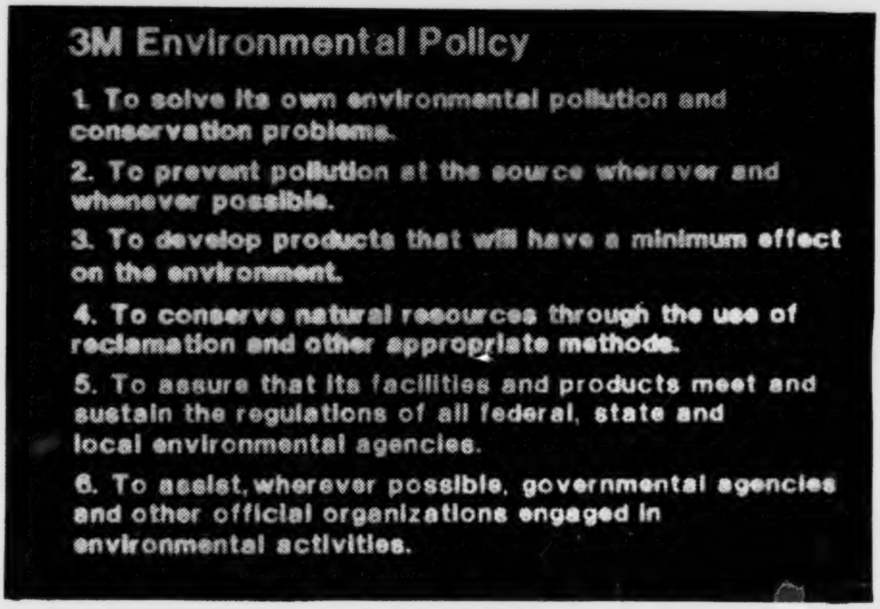
In 1985, on a world-wide basis we had sales of nearly $8 billion. In Canada, our sales exceeded $400 million with a good portion of this in the form of export business.

As a company, we sell over 40,000 different products and we like to say that, each day close to half of the world's population benefits in some way from our 3M products. Around the globe, millions of people watch television recorded and broadcast on our "Scotch" Brand Video Tape; find their way with the help of "Scotchlite" Reflective Road Signs; take comfort from 3M Health Care and Safety products; smooth out the rough edges with 3M Sandpaper; or hold things together with 3M Adhesives and "Scotch" Brand Tapes.

As a company, we have established a reputation for innovation in the development of new products. In fact, as a corporate goal, we look for 25% of our sales in any one year to come from products that have been introduced in the last five years.

It is because we are a new products oriented company, where products and processes are constantly being invented or modified, that it has been somewhat easier for us to incorporate pollution prevention into our activities.

While that may be true, the fact that we have Manufacturing Plants in several locations in the U.S., in over 40 Countries around the world and in four locations in Canada, complicates compliance with Environmental Regulations.



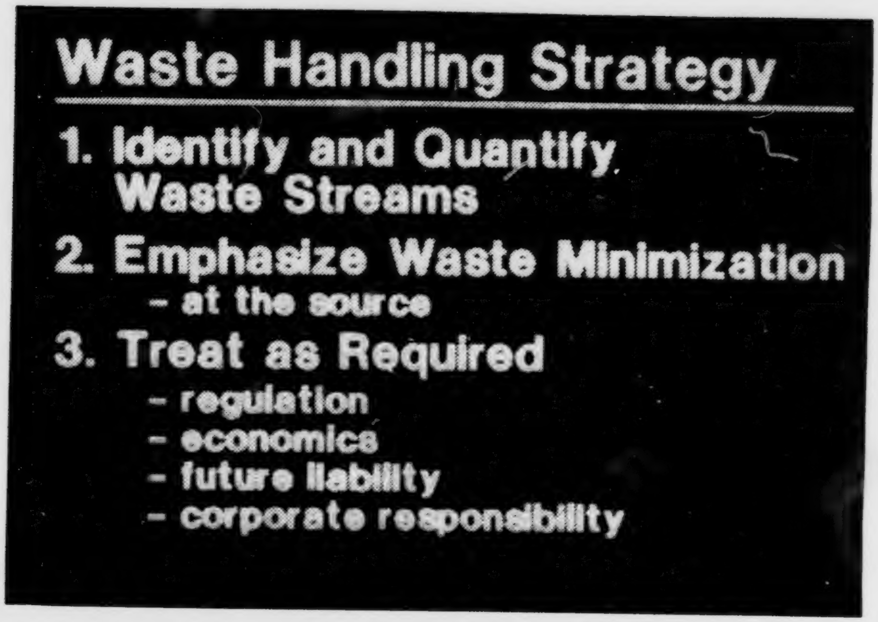
3M Environmental Policy

1. To solve its own environmental pollution and conservation problems.
2. To prevent pollution at the source wherever and whenever possible.
3. To develop products that will have a minimum effect on the environment.
4. To conserve natural resources through the use of reclamation and other appropriate methods.
5. To assure that its facilities and products meet and sustain the regulations of all federal, state and local environmental agencies.
6. To assist, wherever possible, governmental agencies and other official organizations engaged in environmental activities.

SLIDE 2

Corporate Management recognized this back in 1975 and provided a set of guidelines to work by - our Environmental Policy Statement. Points 5 and 6 essentially say that we will comply and we will cooperate.

But points 1 through 4 go considerably beyond this and lay out a strategic approach of solving our own problems, conserving resources and reducing or preventing pollution at the source.



Waste Handling Strategy

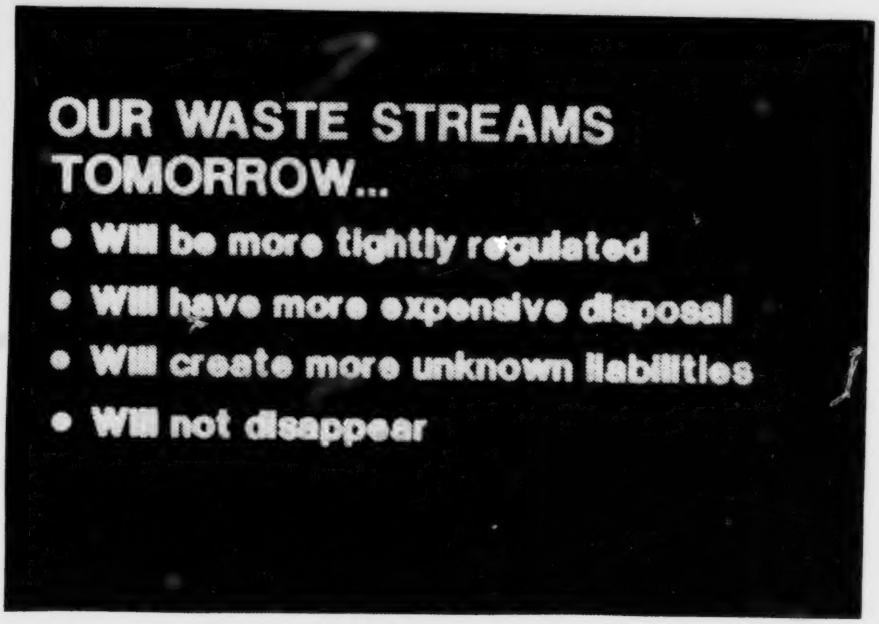
1. Identify and Quantify Waste Streams
2. Emphasize Waste Minimization
   - at the source
3. Treat as Required
   - regulation
   - economics
   - future liability
   - corporate responsibility

SLIDE 3

This policy carries over to our waste handling strategy. Here again, emphasis is on minimizing waste at the source.

But we also recognize that treatment of existing waste streams may be required by regulation, reduction of potential future liabilities or just good corporate citizenship.

Our waste handling strategy obviously applies to all forms of pollution: air, water, and solids.



OUR WASTE STREAMS TOMORROW...

- Will be more tightly regulated
- Will have more expensive disposal
- Will create more unknown liabilities
- Will not disappear

SLIDE 4

One thing is certain, our waste stream tomorrow will be:
- more tightly regulated;
- more expensive to dispose of;
- create more unknown liabilities;
- will not disappear.

A major part of our waste handling efforts involves minimizing waste. We reckon that without the effects of this program over the past eleven years, the amount of waste we generate today would be twice what it actually is.

eliminate
pollution
at
its

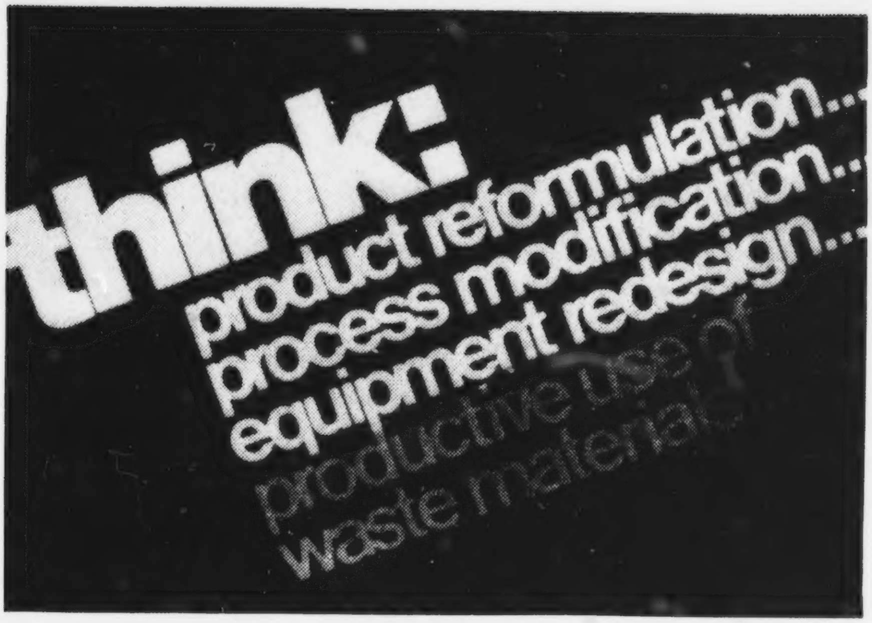
SLIDE 5

The heart of the 3P program is in preventing pollution or waste at the source so that treatment at the end of the manufacturing process is not necessary.

Source prevention applies not only to the process for making a product, but also to the product itself. We want to make sure that after our product leaves our manufacturing locations, that it does not become a source of pollution for our customer down the road.

Attacking the problem at the source is not a new idea. It has been around for many years - but generally used on a piecemeal basis. The unique aspect of the 3M - 3P program is that it applies the pollution prevention concept on a comprehensive, company-wide basis around the world.

There are four basic ways to prevent pollution at the source:



think:
product reformulation...
process modification...
equipment redesign...
productive use of
waste materials

SLIDE 9

1. Develop non-polluting products or reformulate existing products. This is simply done by substituting non-polluting materials for ingredients that are pollutants.

   A good example of this is our effort to substitute water-based adhesives for those that contain solvents. These solvents are pollutants because, untreated, they contribute to the formation of ozone in the atmosphere.

2. Modify production operations. For example, convert to a solventless coating process as we have in our Perth, Ontario location. Or change from a batch to a continuous process in order to reduce peak discharges.

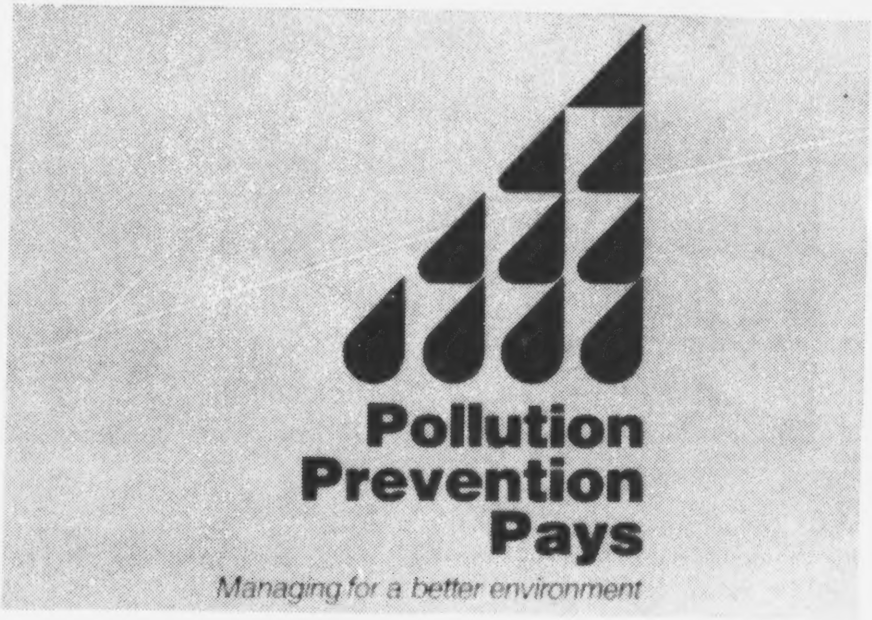
3. Redesign equipment used in a manufacturing process. For example, at one of our plants, we converted a boiler so that it could burn solvent laden exhaust from a coater, thereby eliminating add on pollution control equipment, in addition to providing significant savings per year in energy costs.

4. Recover and recycle waste products. As an example, at one of our plants, a film developing unit generated waste water containing 1,1,1-trichloroethane.

   A Decanter System was installed to recover the developer for later distillation and recycling. The Decanter System cost $4,000 but produced cost savings of over $20,000 over the first four years of operation.

3M has many examples of successful projects in all four basic categories - with cost savings ranging from a few thousand to hundreds of thousands of dollars.

Our most prolific categories have been reformulation and recycling. But we recognize that for other companies, their best opportunities may lay in a different set of categories. It is clear however that the four categories are the same, regardless of products or processes.



Pollution
Prevention
Pays

Managing for a better environment

SLIDE 10

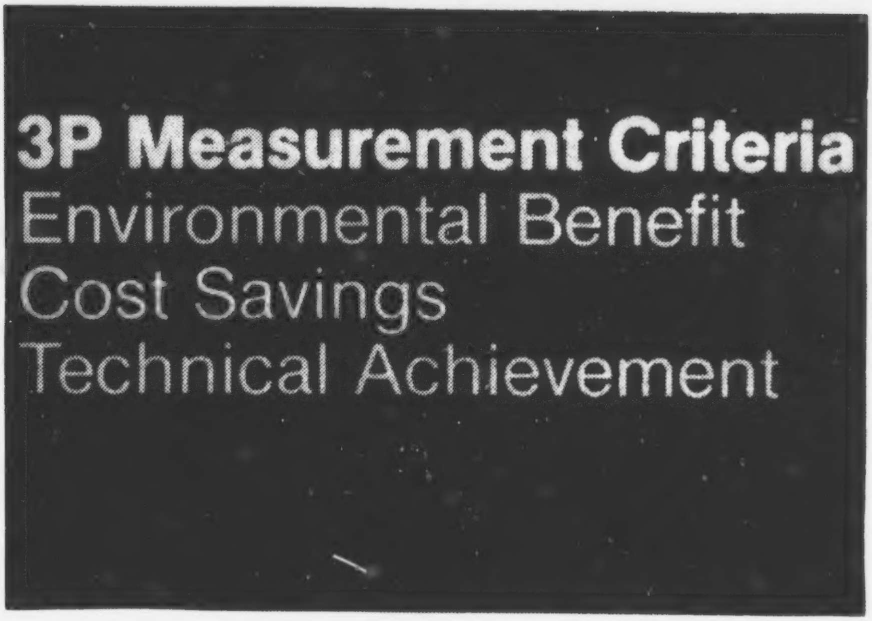
And now for a look at how the 3P program works.

Above all, it is a corporate-wide program fully endorsed by management at all levels. Our Chief Executive Officer is one of its biggest supporters. All of our operating divisions and our subsidiary operations are encouraged to participate.

It is mainly directed at the company's technical employees in Manufacturing, Engineering and our Laboratories. They are responsible for our products and processes and thus the ones most able to work on pollution prevention at its source.

Working in their own specialty areas, doing the work they know best, they are asked to implement pollution prevention concepts in their everyday activities.

When they believe they have made a worthwhile accomplishment, they submit their effort to a 3P Coordinating Committee of Laboratory, Engineering and Manufacturing representatives for review.



3P Measurement Criteria
Environmental Benefit
Cost Savings
Technical Achievement

SLIDE 11

Each submission is judged on the following criteria:

1. It must result in an environmental benefit that can be quantified, such as the amount of pollution prevented.
2. It must produce a cost savings for the company.
3. It must demonstrate a technical achievement or an innovative approach above and beyond standard engineering or manufacturing procedures.

If the idea meets with peer approval, then and only then is it accepted as a 3P project.

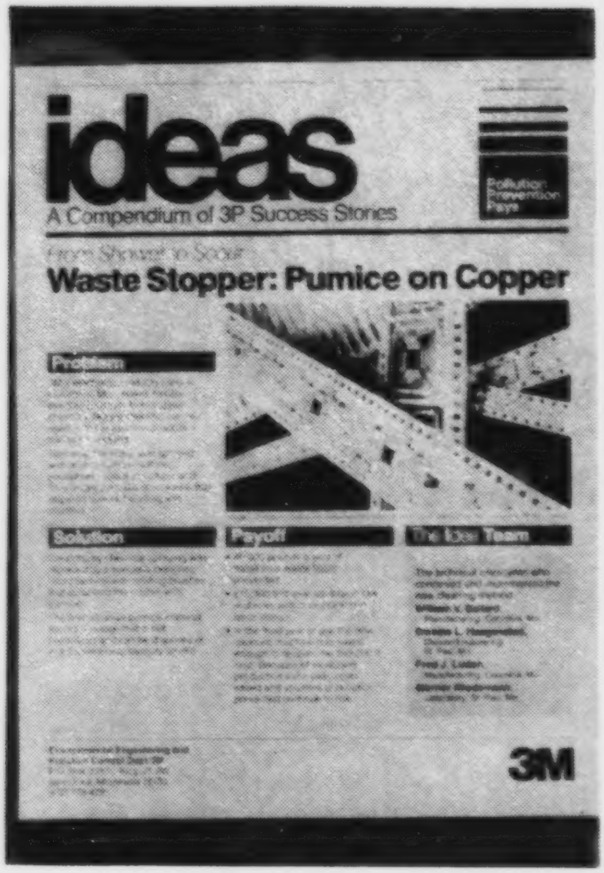
Contributors to the program have proven to be among 3M's most creative technical employees and this recognition serves to reinforce their reputations and contribute to their career growth. Recognition is the only immediate award and we avoid prizes or cash awards that smack of contests or promotions.

Because of strong management support, our annual management review take note of which divisions are doing the most, and the least, to produce 3P projects.

The net result is that the Program continues to grow and the results get better each year.

A significant part of the 3P Program involves communication, both inside and outside the company.

Internal communications have concentrated on sharing 3P success stories with others in 3M around the world. These one-pagers combine technical, economic and environmental information in an easy-to-read form with a little humour thrown into the headline.



ideas

A Compendium of 3P Success Stories

Pollution Prevention Pays

From Shower to Scour

Waste Stopper: Pumice on Copper

Problem

Solution

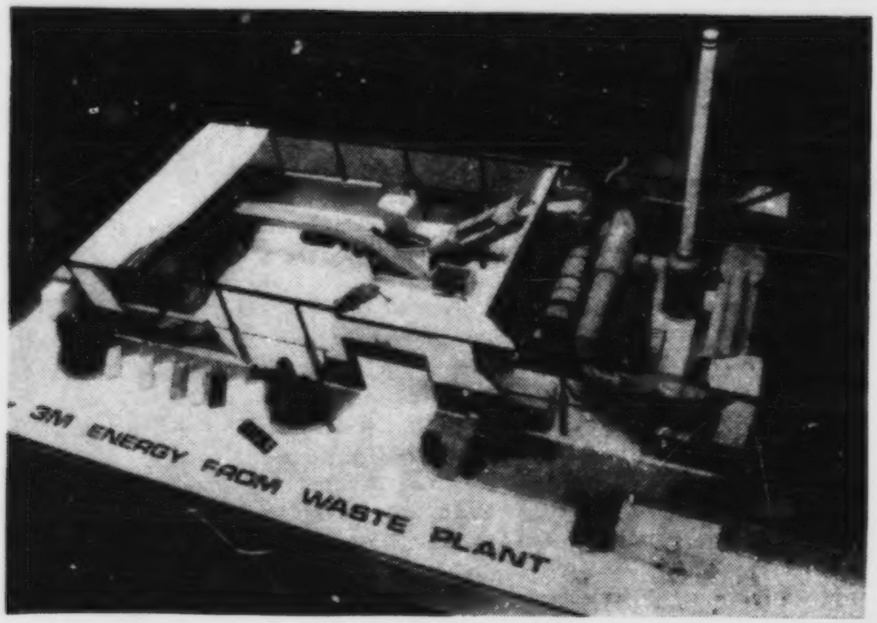
Payoff

The Idea Team

3M

SLIDE 12

This one, "From Shower to Scour Waste Stopper: Pumice on Copper" - describes a project in which copper circuits are now cleaned by scrubbing with pumice rather than by spraying with corrosive acids. The result is non-hazardous waste instead of 40 pounds per year of hazardous waste, and a fast 2-1/2 year payback on investment.



SLIDE 13

Another example involves a project initiated at our 3M Canada Headquarters in London, Ontario. This project, an Energy from Waste installation, has attracted a good deal of publicity in the area, and is an excellent example of how serious environmental problems can be reduced within the community.

The genesis of the project came while considering how to control a Tape Oven Exhaust that produced an odour under certain climatic conditions. At the same time we were very conscious of the amount of dry, non-hazardous waste we were sending each day to the municipal landfill site.

The solution---an Energy from Waste Plant that will use our tape exhaust stream and dry waste material as fuel augmented by similar waste from surrounding Industry.

As a result we expect to eliminate the odour, reduce the number of trucks of waste on London streets and, of course, extend the life of the landfill site.

With this project we will not only control our waste but the heat generated by the incineration process will make us largely self-sufficient in the generation of steam for our manufacturing operations.

The 3P mentality and the solid support the concept has within the company eased the acceptance of the project at 3M even in the face of some community concerns.

While not related to our project in any way, a PCB problem within the immediate area of our plant affected the outlook of our neighbours as did an earlier EFW proposal by a local hospital which created wide media and local interest and concern.

Again the 3P concept provided us with sensitivity to the needs and concerns of our employees and neighbours alike and allowed us to develop an information program that provided all interested parties with all the information they needed as to the scope and implications of the project.

In fact the very existence of our 3P Program was used as evidence in our submission to the Ministry of the Environment for approval of the incinerator as an indication of the culture in place at 3M that motivated us to propose such a project.

Clearly we believe strongly in the 3P concept. And, we do not hesitate to "sell" the concept to others because we believe industry can establish a leadership position in the environmental area - a position that industry has shunned too often in the past.

The 3P concept has been adopted by many others - organizations, companies, and even the United Nations. The U.N. has been most interested in the 3P concept because it represented, in their estimation, the only affordable approach to environmental protection for the less developed countries.

Those factors that make the 3P approach valuable to industry in the developed countries of the world apply equally well to those countries who are still struggling with the basics of existence.

In summary, since the Program's inception in 1975, 3P projects have saved over a quarter of a billion dollars world-wide for 3M.

These costs reflect pollution control facilities that did not have to be built, reduced pollution control operating costs, reduced manufacturing costs, and retained sales of products that might have been taken off the market as environmentally unacceptable.

We expect these cost savings to continue to grow as more and more of our people begin to think of new ways to prevent pollution.

The Program world-wide has yielded equally good results from an environmental standpoint as from a monetary viewpoint.

Tons of air pollutants and water pollutants have been eliminated from the environment in the area of our manufacturing locations.

These 3P results are an illustration of what can be done. The encouraging word today is that many companies are in fact eliminating or reducing pollution at source.

They are demonstrating that there is, indeed, a payoff in managing for a better environment and in preventing pollution at its source.

Pollution
Prevention
Pays

Managing for a better environment

SLIDE 14

THE BENEFITS OF
REDUCING LEAD IN U.S. DRINKING WATER

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The Safe Drinking Water Act (SDWA), passed by the U.S. Congress in 1974, requires the U.S. Environmental Protection Agency (EPA) to protect public health by setting drinking water standards for public water supplies.* Two levels of protection are described in the SDWA. Primary drinking water regulations, applicable only to public water systems, specify contaminants that may have an adverse effect on human health and, for each contaminant, set either a maximum contaminant level (MCL) or a treatment technique requirement. Secondary drinking water standards are non-enforceable recommendations concerning the aesthetic quality of drinking water, e.g., taste or smell.

The National Primary Drinking Water Regulations (NPDWR) were first promulgated at the end of 1975. EPA revises those regulations by setting maximum contaminant level goals (MCLGs) and related MCLs. MCLGs are non-enforceable health-based goals, intended to protect against known or anticipated adverse health effects, with an adequate margin of safety. MCLs are enforceable limits, to be set as close as feasible to the MCLG; feasibility includes cost and technological constraints. MCLs are proposed at the same time as the MCLGs.

On November 13, 1985, EPA proposed National Primary Drinking Water Regulations (NPDWR) to set MCLGs for 24 synthetic organic chemicals, 10 inorganic chemicals, and 6 microbiological parameters in drinking water; these substances are listed in Table 1. The proposed MCLGs for probable human carcinogens were set at zero, and MCLGs for other substances were based upon chronic toxicity and other data.

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* Defined in the Act as water systems serving 25 or more people or having at least 15 service connections.

Lead is included among the inorganic substances proposed for regulation in the NPDWR. The current MCL for lead is 50 micrograms of lead per liter of drinking water (ug/l);* the proposed MCLG is 20 ug/l.

Summary of Study

This analysis estimates some of the benefits that will result from the proposed reduction in the MCL for lead in community drinking water supplies. There are two primary categories of benefits in this paper: the public health benefits of reduced lead exposure and reduced materials damages relating to the phenomenon of lead's presence in drinking water -- as a corrosion by-product. In addition, because the calculation of health benefits depends on the extent of human exposure, another section presents the available data on the occurrence of lead in public water supplies, and presents estimates of the population exposed to drinking water exceeding the proposed MCL of 20 ug/l.

This analysis estimates the annual benefits for one sample year, 1988, of lowering the MCL from 50 ug/l to 20 ug/l. That one year was chosen because environmental lead levels will have

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* This is equivalent to and can be alternately stated as 0.05 milligrams per liter (mg/l), 0.05 micrograms/gram (ug/g), or 50 parts per billion (ppb).

TABLE 1. Substances Included in the 1985 Proposed National Primary Drinking Water Regulations (MCLGs)

A. Synthetic Organic Chemicals

1. Acrylamide
2. Alachlor
3. Aldicarb, Aldicarb sulfoxide and Aldicarb sulfone
4. Carbofuran
5. Chlordane
6. Dibromochloropropane
7. o-,m-Dichlorobenzene
8. cis- and trans-1,2 Dichloroethylenes
9. 1,2-Dichloropropane
10. 2,4-D
11. Epichlorohydrin
12. Ethylbenzene
13. Ethylene dibromide
14. Heptachlor and Heptachlor epoxide
15. Lindane
16. Methoxychlor
17. Monochlorobenzene
18. Polychlorinated biphenyls
19. Pentachlorophenol
20. Styrene
21. Toluene
22. Toxaphene
23. 2,4,5-TP
24. Xylene

B. Inorganic Chemicals

1. Arsenic
2. Asbestos
3. Barium
4. Cadmium
5. Chromium
6. Copper
7. Lead
8. Mercury
9. Nitrate and Nitrite
10. Selenium

C. Microbiological Parameters

1. Total Coliform Bacteria
2. Turbidity
3. Giardia
4. Pathogenic Viruses
5. Legionellae
6. Heterotrophic Bacteria
7. Treatment Technique Requirements
    a. Mandatory Filtration and Disinfection of Surface Water for Microorganisms
    b. Mandatory Disinfection of Ground Water

stabilized following EPA's 1984 phasedown of lead in gasoline.*

For comparability, all monetary values are expressed in 1985 dollars, using fixed-weighted price indexes for the gross national product (Table B-4), from the 1986 Economic Report of the President to Congress.

1. The Occurrence of Lead in Public Drinking Water

Lead occurs in drinking water primarily as a corrosion by-product; its sources are the materials used in the distribution and residential plumbing systems (cf sources as diverse as the EPA Air Quality Criteria Document for Lead, 1986; Craun and McCabe, 1975; Kuch and Wagner, 1983; Lead in (British) Drinking Water, 1977; etc). Pipes and solder containing lead are corroded by water, and lead levels at the user tap are much higher than those found at the treatment plant. While the presence of lead service pipes and mains is relatively restricted geographically in the U.S., the use of lead solder (and flux) is ubiquitous. And the combination of copper pipes with solder containing lead found in most households can result in high lead levels** -- levels exceeding the current MCL, even with fairly non-corrosive waters (e.g., Nielson, 1976). In particular, newly-installed solder is easily dissolved, and people living in new housing are especially at risk of high levels of lead in the drinking water (Sharrett et al., 1982; Murrell, 1985).

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* Specifically, this analysis measures effects given the conditions on January 1, 1988, when EPA's proposed ban on leaded gasoline will not yet have taken effect. However, even if EPA promulgates the ban, the estimates in this report will not change significantly.

** This results from galvanic corrosion, which is the corrosion that occurs when 2 metals, with different electro-chemical potential, are in the same environment.

We used several sources of data to develop a national profile of exposure to lead from community drinking water supplies.* These included the 1978 (U.S.) Community Water System Survey, the (U.S.) National Inorganics and Radionuclides Survey (conducted by EPA), the (U.S.) Federal Reporting Data System (EPA's drinking water compliance data base), data from the WaterTest Corporation (a private water testing company), and data from the Culligan Company (a water softening firm) analyzed for EPA in 1979-81 by J. Patterson. Based upon the observations contained in these data sets, we estimate that at least 28.5 million people (lower bound: 20.8 million) currently receive water that has over 20 ug/l of lead.

To this must be added the inhabitants of housing built within the past 24 months. Many studies have shown that new solder can release significant amounts of lead into water, even exceeding the current MCL. While corrosive waters have the highest lead levels, relatively non-corrosive waters can also leach significant amounts of lead. The highest lead contamination levels occur with the newest solder (i.e., during the first 24 months after installation), but lead levels can remain elevated for five years (e.g., Sharrett et al., 1982; Lassovszky, 1984).

There were 1.7 million new housing starts and permits (public and private) in 1983 and 1.8 million in 1984.** Assuming that housing typically takes six months to a year from permit to potential occupancy, there are currently a total of 3.5 million new housing units (i.e., < 24 months). The Statistical Abstract of the United States (1985) indicates that the average household contains 2.73 individuals (Table 58). Multiplied together, a total of 9.6 million people currently are potentially at risk of lead contamination in their drinking water from newly-installed lead solder.

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* The occurrence data we used relate to the approximately 60,000 community water systems that serve about 219 million people.

** Survey of Current Business, U.S. Department of Commerce - Bureau of Economic Analysis, 1985; Table on New Housing Construction.

Combined, at least 38.1 million people (lower bound: 30.4 million)* using public water supplies currently receive water that exceeds the proposed MCL. We consider this a low estimate because:

- we have not considered the potential exposure of occupants in housing built within the past 2-5 years (who probably remain at greater risk of elevated lead levels);
- many samples in the data base were taken from the distribution system and not from within a private residence (biasing the results downwards);
- at least two data sources may contain biases that underestimate exposure; and
- our data are from running samples, while many people consume water that is closer to standing samples (and which most likely contains higher concentrations of lead).**

In addition, we have not included any data from the 30-40 million users of private and non-community water supplies which, because those systems are not covered by the SDWA, need not comply with EPA's drinking water standards and monitoring requirements (and so may be more likely to have higher contamination levels).

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* This analysis includes only an estimate and a lower bound. Our data do not provide a basis for an upper bound estimate.

** Water that has been standing in pipes has a greater opportunity for lead to leach into it and, therefore, is more likely to contain higher lead levels.

Our estimates of the health benefits associated with this proposed rule rely on the data collected for the Second (U.S.) National Health and Nutrition Examination Survey (NHANES II), a 10,000 person representative sample of the U.S. non-institutionalized population, aged 6 months to 74 years. That data base is available from the (U.S.) National Center for Health Statistics and data from it have been published often (e.g., Annest et al., 1980 and 1982; Mahaffey et al., 1982; Pirkle and Annest, 1984).

Our assumptions on the relationship between water lead levels and blood lead levels are taken from the Water Criteria Document for Lead (1985). That document assumes a linear relationship, with different constants for children and adults. Those formulae are:

(for children) PbB* = 0.16** x intake of lead from water

(for adults) PbB* = 0.06** x intake of lead from water

Alternative assumptions (e.g., Richards and Moore, 1982 and 1984) could indicate that we have underestimated exposure -- and consequently underestimated benefits -- by a factor of 3-5.

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* PbB = blood lead level

** These constants have a unit of micrograms-of-lead/deciliter-of-blood per microgram-of-lead-in-water/day, or ug/dl per ug/day.

2. Benefits of Reducing Children's Exposure to Lead

Elevated blood-lead levels have long been associated with neurotoxicological effects and many other pathological phenomena: an article on lead's neurotoxicity was published as early as 1839, on anemia in the early 1930s, on kidney damage in 1862, and on impaired reproductive function in 1860. From an historical perspective, lead exposure levels considered acceptable for either occupationally-exposed persons or the general population have been revised downward steadily as more sophisticated biomedical techniques have shown formerly-unrecognized biological effects, and as concern has increased regarding the medical and social significance of such effects. In the most recent downward revision of maximum safe levels, the Centers for Disease Control (CDC) lowered its definition of lead toxicity to 25 micrograms of lead per deciliter of blood (ug/dl, the standard measure of blood lead level) and 35 ug/dl of free erythrocyte protoporphyrin (FEP). The present literature shows biological effects as low as 10 ug/dl (for heme biosynthesis) or 15 ug/dl (for renal system effects and neurological alterations); indeed, some effects (e.g., elevated levels of a potential neurotoxin* or stature effects, Angle et al., 1982; Schwartz et al., 1986, etc.) have exhibited no threshold so far.

There is no convincing evidence that lead has any beneficial biological effect in humans (Expert Committee on Trace Metal Essentiality, 1983).

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* ALA, or aminolevulinic acid.

Elevated blood-lead levels have been linked to a wide range of health effects, with particular concern focusing on young children. These effects range from relatively subtle changes in biochemical measurements at 10 ug/dl and below, to severe retardation and even death at very high levels (80-100 ug/dl). Lead can interfere with blood-forming processes, vitamin D metabolism, kidney function, neurological processes and reproductive functions in both males and females. In addition, the negative impact of lead on cognitive performance (as measured by IQ tests, performance in school, and other means) is generally accepted at moderate-to-high blood-lead levels (30 to 40 ug/dl and above), and several studies also suggest cognitive effects at much lower levels; changes in electroencephalogram readings, for instance, are detectable at levels as low as 10 ug/dl. For many subtle effects, our data represent the limits of detectability of biochemical or other changes, and not thresholds for effects.

For children's health effects, we estimated two categories of benefits: medical care for children exceeding the lead toxicity level set by the Centers for Disease Control (25 ug/dl, when present in combination with FEP levels > 35 ug/dl) and cognitive effects. We developed two alternative methods for valuing the potential cognitive damage resulting from exposure to lead. The first of these two alternatives involves assessing the costs of compensatory education to address some of the manifestations of the cognitive damage caused by lead as a proxy measure for the damage itself. The second relates to one specific indication of that cognitive damage -- potential IQ point loss, and includes a calculation of decreased expected future earnings as a function of IQ point decrement. These estimates are conservative because, for instance, they do not include many major categories of pathophysiological effects (e.g., renal damage), nor do either the medical costs or the compensatory education costs consider any lasting damage not reversed by medical treatment or compensatory education, nor do they attribute many benefits to reducing lead levels in children whose blood lead levels would be below 25 ug/dl even in the absence of the rule.

To estimate reductions in medical care expenses, we used published recommendations (Piomelli et al., 1984) for testing and treating children with blood lead levels above 25 ug/dl. Such treatment, we estimate, costs about $950 per child over 25 ug/dl (1985 dollars). (This average reflects lower costs for most of these children, but much higher costs for the subset requiring chelation therapy.)

The estimates for compensatory education assumed three years of part-time compensatory education (de la Burde and Choate, 1972 and 1975) for 20 percent of the children above 25 ug/dl, averaging about $2,800 per child above that blood lead level (1985 dollars), based upon data from Kakalik et al., 1981.

There is extensive literature examining the relationships between schooling, IQ, demographic variables and earnings (ICF, 1984). We used the results of that literature to calculate the effect of the IQ point losses that can occur as a part of the cognitive damage caused by lead exposure upon expected future earnings: one IQ point can directly and indirectly affect earnings by 0.9 percent. The studies of cognitive damage presented in the Air Quality Criteria Document for Lead (U.S. EPA, 1986) show evidence that blood lead levels of 15-30 ug/dl can be associated with IQ losses of 1-2 points, blood lead levels of 30-50 ug/dl can be associated with IQ losses of 4 points, and over 50 ug/dl of blood lead can correlate with losses of 5 points. We used data from the Census Bureau on expected future lifetime earnings, deferred for 20 years* at a 5 percent real discount rate, and then annualized the potential damage to yield estimated benefits benefits from reduced exposure to lead. This alternative method for valuing some of lead's cognitive damage indicated that the U.S. could save $1,040 per child brought below 15 ug/dl; $2,600 per child brought below 30 ug/dl; and $2,850 per child brought below 50 ug/dl by reducing lead in drinking water (1985 dollars).

In sum, this proposed rule will produce benefits of $7.7 million annually in avoided medical expenses; $22.7 million per year in reduced compensatory education costs; and $151.7 million per year in increased lifetime earnings, based upon sample year 1988; these estimates are in 1985 dollars. Note that compensatory education and affected earnings are alternative methods for valuing aspects of the cognitive damage caused by lead.*

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* These costs are deferred because those suffering the effects are children and will not enter the work force for up to 20 years. Obviously, using the largest deferral period (20 years) reduces the value of the benefit and reduces our benefit estimate, whereas 8-or 10-year-old children may begin working within 8 years and so would have a much shorter deferral period. This biases our estimates downward.

In addition, there are two other categories of health effects (lead's adverse affect upon children's growth and potential fetal effects) that we did not monetize. However, this rule could prevent 36,400 children from growth decrements and 622,000 fetuses from being exposed to potentially dangerous lead levels. The fetal effects are particularly important, because several recent studies have shown lead levels associated with various negative pregnancy outcomes (e.g., Moore, 1982; Wibberly et al., 1977), with inhibited post-natal growth and development (e.g., Bornschein, 1986; Bellinger, 1985 and 1986; Dietrich et al., 1986), and even with Sudden Infant Death Syndrome (Erickson et al., 1983).

3. Blood-Pressure-Related Benefits and Other Adult Health Effects

Lead has long been associated with elevated blood pressure, but until recently most of the studies have focused only on hypertension and relatively high lead levels typically found only in those occupationally exposed to lead. Several recent studies, however (e.g., Pirkle et al., 1985; Harlan et al., 1985; Pocock, 1984 and 1985), have found a continuous relationship between blood lead and blood pressure, and show a strong relationship that has proved robust in the face of exhaustive statistical tests involving many possible confounding factors and alternative specifications of the model. These recent studies may help to explain the inconsistent findings of association in analyses conducted over the past 30 years on the relationship between soft water and cardiovascular disease rates (cf. Comstock, 1985).

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* This is a conservative assumption. There is a strong rationale for seeing these effects as additive.

To calculate the benefits of reduced lead exposure, we used logistic regression equations to predict how an MCL of 20 ug/l would affect the number of hypertensives. These estimates cover only males aged 40 to 59, because the effect of lead on blood pressure appears to be strongest for men and because estimates for that age range are not confounded by a strong covariance between age and both blood pressure and blood lead. Our estimates rely upon data from the NHANES II and cardiovascular disease coefficients from the Framingham Study (McGee et al., 1976) and Pooling Project (1976), as confirmed by Levy et al., 1984.

We estimate that the rule will reduce the number of male hypertensives between the ages of 40 and 59 by 118,400 in 1988. We valued reductions in hypertension based on estimates of the costs of medical care, medication, and lost wages; they yielded a value of $250 per year per case of hypertension avoided (1985 dollars).

We also estimated how reductions in blood pressure would affect the incidences of various cardiovascular diseases, based on our projections of changes in blood pressure as a result of the rule and estimates of the relationships between blood pressure and heart attacks, strokes, and deaths from all causes. The latter estimates were derived from several large epidemiological studies, primarily the Framingham study. Because those studies included very few nonwhites, we further restricted our estimates to white males aged 40 to 59. The basis of most of the medical costs is presented in Hartunian et al., 1981. We adjusted the cost-of-illness estimates contained there in three ways to reflect current conditions. First, we inflated them to 1985 dollars using data from the 1986 Economic Report of the President to Congress. Second, we adjusted the costs to reflect changes and improvements in treatment, including the tripling in the incidence rate of coronary bypass operations that occurred between 1975 and 1982. Third, Hartunian used a 6 percent real discount rate to present value future expenditures, while our analysis uses a 10 percent real discount rate.

We valued reductions in heart attacks and strokes based on the cost of medical care and lost wages for nonfatal cases (the fatalities from heart attacks and strokes were included in the estimate of deaths from all causes). That procedure yielded benefits of $65,000 per heart attack and $48,000 per stroke avoided (1985 dollars) for the 370 heart attacks and 75 strokes avoided in 1988 because of this proposed rule. It is important to note that these estimates do not account for any reductions in the quality of life for the victims of heart attacks and strokes (e.g., the partial paralysis that afflicts many stroke victims).

Valuing reductions in the risk of death is difficult and controversial, with a wide range of estimates in the literature. EPA's policy guidelines (U.S. EPA, 1984), for example, suggest a range of $400,000 to $7 million per statistical life saved. For our point estimate, we used a value from the lower end of that range, $1 million per case. The benefits of reduced mortality dominate our estimates of total blood-pressure-related benefits, and total $370 million in 1988 for the 370 avoided deaths in that year. Altogether, the monetized benefits of reducing adult male exposure to lead by reducing the MCL for lead in drinking water total $427.3 million per year (in 1985 dollars), using 1988 as a sample year.

In addition, because lead crosses the placental barrier and is a fetotoxin, pregnant women exposed to lead are at risk of complications in their pregnancies and damage to the fetus. Among these adverse effects are higher miscarriage rates and spontaneous abortions (fetal effects are discussed above, under children's health effects). While we have not monetized any of these reproductive effects, 622,000 pregnant women per year probably receive water that exceeds the proposed standard of 20 ug/l, and would benefit from the proposed rule. Lead-induced effects on male reproductive functions have also been discussed in the scientific literature but are not included in this report.

4. Benefits of Reduced Materials Damage

A third category of monetized benefits relates to the phenomenon of lead's presence in drinking water: it is a product of the corrosive action of water upon the materials of the distribution and residential plumbing. For the most part, therefore, treatment processes used to reduce high levels of lead in drinking water are the same as treatment processes used to reduce the corrosion potential of the water. Reducing corrosion damage will produce substantial benefits to water utilities, their rate-paying customers, and building owners.

Published estimates of the costs of corrosion damage range from $12 to $46 per person per year (1985 dollars), and are summarized on Table 2. Estimates of the costs that can be avoided by corrosion control measures range from 20-50 percent of total damage. Our point estimate of avoidable corrosion costs (i.e., the benefits of corrosion control) is $8.50 per capita annually (1985 dollars). For comparison, estimates of average corrosion treatment costs range from under $1 per person per year (based upon the experience in Boston and Seattle, cities currently treating their highly corrosive waters) to almost $5 per person per year (based upon the highest treatment costs presented in the ODW cost report).* As a point estimate, we assumed per capita annual treatment costs of $3.80 (1985 dollars).

Estimates of the extent of corrosive water also vary. The most commonly accepted profile is that developed by the U.S. Geological Survey in the early 1960s, which identified the Northeast, Southeast, and Northwest sections of the country as having the softest and most corrosive waters (Durfor and Becker, 1964a and 1964b). The combined populations of those states are 49.6 million people (1980 census). That figure, multiplied by $8.50 per person, yields annual benefits from reduced corrosivity of $421.6 million (1985 dollars).

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* The range, however, is quite wide and highly sensitive to system size. These represent average costs. In some very small systems (i.e., serving 25-100 people), costs may be many times higher.

TABLE 2. Estimates of Annual Per Capita Corrosion Damage (1985 dollars)

Studies	Estimated Annual Corrosion Damage (per capita)			Corrosion Damage Avoidable Through Water Treatment	Annual Per Capita Benefits of Corrosion Control	Assumptions/Notes
	Distribution Systems	Residential	Total			
Kennedy Engineers (1973)	$5.57	--	$16.71*	30%*	$5.01*	We assumed 30% potential reduction in corrosion damage and that distribution costs were one-third of total costs.
Hudson & Gilcreas (1976)	$8.68*	--	$26.04*	50%	$13.02*	They did not include increased operating costs. Per capita estimate assumes 200 million people are served by public water systems. We assumed that distribution costs were one-third of total costs.
Kennedy Engineers (1978)	--	$30.87*	$46.30*	20%	$9.26*	They calculated $6.17 per capita in savings to residence owners. We assumed residential costs were two-thirds of of total costs.
Bennett et al. (1979) (cited in Ryder, 1980)	$9.40	--	$28.20*	20%	$5.64*	We assumed that 200 million people are served by public water systems and that distribution costs were one-third of total costs.
Energy & Environmental Analysis (1979)	$3.98	$7.97	$11.95	38%	$4.54	This is an admitted underestimate: it includes only damage to pipes.
Ryder (1980)	$1.17	$22.19	$23.36	25%	$5.84	Ryder ascribed 95% of corrosion damage to private owners
Kirmeyer & Logsdon (1983)	--	$23.60*	$35.40*	40%	$14.16*	We assumed residential costs are two-thirds of total damage.
					AVERAGE $8.21 W/OUT EEA $8.82	

* These estimates have been calculated by the authors of this paper based upon assumptions that are not included in the published articles.

5. Summary of Benefits of Reduced Lead in Drinking Water

Our analysis of reducing the MCL for lead from 50 ug/l to 20 ug/l indicates that the monetized annual benefits are large: $879.3 to $1,008.3 million (1985 dollars) for sample year 1988 (lower bound: $806.2 to $889.7 million). In addition, there are numerous health benefits of reduced exposure to lead that we have not monetized. The annual monetized benefits are summarized in Table 3, and the non-monetized benefits are presented in Table 4.

Based upon the latest cost estimates used by the Office of Drinking Water (USEPA, 1984),* the benefits exceed the costs by 7:1 (using the lower-bound estimate of occurrence, also 7:1). Expressed differently, lowering the MCL to 20 ug/l will produce annual net benefits of about $800 million in 1988 (using the lower-bound estimate of occurrence, $700 million).

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* These calculations use preliminary EPA Office of Drinking Water cost estimates. Costs and net benefits will be discussed more extensively in other documents associated with this rulemaking.

TABLE 3. Summary of Annual Monetized Benefits of Reducing the Lead MCL from 50 ug/1 to 20 ug/1 (1985 dollars) for Sample Year 1988

Estimated population exposed to drinking water exceeding proposed MCL	38.1 million* (lower bound: 30.4 million)
Children's health benefits	
-reduced medical costs	$7.7 million
-reduced costs of cognitive damage	
Method 1 - compensatory education	$22.7 million
Method 2 - decreased future earnings	$151.7 million
TOTAL: Method 1	$30.4 million
Method 2	$159.4 million
Adult health benefits (males only)	
-reduced hypertension savings (males, aged 40-59)	$29.6 million
-savings from fewer heart attacks (white males, aged 40-59)	$24.1 million
-savings from fewer strokes (white males, aged 40-59)	$3.6 million
-savings from fewer deaths (white males, aged 40-59)	$370.0 million
TOTAL:	$427.3 million
Materials benefits	
-benefits of reduced corrosion damage	$421.6 million
TOTAL ANNUAL MONETIZED BENEFITS	
-Method 1 - using compensatory education	$879.3 million (lower bound: $806.2 million)
-Method 2 - using decreased future earnings	$1,008.3 million (lower bound: $889.7 million)

* Total population served by community water systems: 219 million

TABLE 4. Summary of Annual Non-monetized Benefits of Reducing the Lead MCL from 50 ug/l to 20 ug/l for Sample Year 1988

	Reductions in Numbers of People at Risk
Estimated population exposed to drinking water exceeding proposed MCL	38.1 million* (lower bound: 30.4 million)
Children's health benefits	
- children requiring medical treatment	8,100
- loss of 1-2 IQ points	142,000
4 IQ points	1,500
5 IQ points	23
- children requiring compensatory education	8,100
- children at risk of stature decrement	36,400
- fetuses at risk	622,000
- increased risk of hematological effects	36,400
Adult health benefits	
-cases of hypertension (males, aged 40-59)	118,400
-heart attacks (white males, aged 40-59)	370
-strokes (white males, aged 40-59)	75
-deaths (white males, aged 40-59)	370
-reduced risk to pregnant women (women, aged 15-44)	622,000
-reduced risk of reproductive effects (women, aged 15-44)	34,000

* Total population served by community water systems: 219 million

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ECONOMIC EFFECTS OF REDUCED FOREST GROWTH ON THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE

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ABSTRACT.

Several recent studies have reported both localized and region-wide decreases in the radial growth rates of several commercially important forest species in the eastern half of United States. These observed reductions in tree growth rates may be related to increases in acid deposition and other man-made air pollutants over the last three decades. In the first part of this study, we review the evidence regarding these reductions in forest growth and, using economic theory, show how these physical changes can impact the production and purchasing decisions of buyers and sellers in timber and primary wood product markets. We then show how standard willingness-to-pay principles can be used to place monetary values on the physical damages caused by air pollution, due to these changes in the behavior of economic agents in affected markets. In the second part of the study, we describe how this information about changes in tree growth can be used in conjunction with existing inventory projection and timber market models to simulate the potential economic effects of acid deposition/air pollution in the United States. Two sets of simulations are conducted. The first set assumes that air pollutants generated in the United States do not damage Canadian forests. The second set of simulations attempts to take into account the potential effects of reduced growth in Canadian forests due to air pollutants generated in the United States and/or Canada. These damages are simulated by increasing Canadian stumpage fees in the Canadian lumber supply functions contained in the timber market model used in the analysis. The final part of the study presents the results of the simulations, quantifying the potential economic effects of acid deposition in the United States and to a limited extent, Canada. Specific attention is focused on the effects of different assumptions regarding the magnitude and geographic distribution of reduced tree growth on timber inventories, stumpage prices and harvest levels, lumber and plywood production and prices in the United States, and on Canadian lumber exports to the U.S. Estimates of the effects of reduced tree growth on the welfare of timber owners and the buyers and sellers of lumber and plywood in the United States are presented, along with information about changes in the welfare of lumber producers in Canada. These results suggest that if increases in Canadian stumpage fees (as a government response to transboundary pollution damage) are not too great, Canadian lumber producers and exporters may actually earn higher profits because of increased demand from the United States for Canadian lumber exports. While

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Canadian consumers would be hurt by higher prices, quantitative effects on this sector and on Canadian timber owners could not be computed due to modeling constraints.

1. INTRODUCTION

This paper has three objectives: 1) to describe the methodological framework that was developed for the United States' National Acid Precipitation Program (NAPAP) to assess the range of potential economic impacts that could occur due to air pollution-induced reductions in forest growth in the eastern United States; 2) to present the results of that analysis, prepared for the 1985 Damage Assessment; and 3) to explore the potential effects of reduced forest growth in the United States and Canada on exports of lumber from Canada to the United States and on the economic well-being of Canadian lumber producers. To meet these objectives, the paper is divided into three major sections. The remainder of Section 1 provides background information about NAPAP and the goals of the 1985 Damage Assessment. It also presents evidence for concern about possible slowdowns in forest growth in the eastern United States. Finally, Section 1 shows how standard willingness-to-pay principles can be used to place monetary values on the physical damages caused by air pollution. Section 2 describes the methodological framework and simulations that were developed to assess the economic impacts of simulated reductions in forest growth, while Section 3 presents the results of these simulations. Finally, Section 4 summarizes the findings of this study.

1.1. NAPAP 1985 Assessment-Overview

NAPAP was created by the Acid Precipitation Act of 1980 (Title VII of the Energy Security Act, P.L. 96-294). Planning for NAPAP commenced in the fall of 1980 and a final plan was completed, after extensive public review, in the summer of 1982. This was supplemented in 1984 by a more detailed Operating Research Plan [1] which called for the execution of several assessments, the first scheduled for 1985, to evaluate the causes, effects and damages resulting from acid deposition. Responsibility for conducting these assessments was specifically given to the Assessments Task Group (Task Group I), which is one of 10 working groups organized within the NAPAP programmatic organization.

The NAPAP 1985 Assessment possessed at least two important characteristics that distinguish it from subsequent, integrated assessments. First, the 1984 NAPAP plan [1] specifically charged Task Group I with estimating the magnitude of the current physical and economic damages caused by acid deposition phenomena in the 1985 Assessment, whereas subsequent assessments were to examine the benefits of (or damages reduced by) specific control options. An important aspect of the damages-oriented focus of the 1985 Assessment that needs to be stressed is that the preliminary damage estimates reported in this study may not be the same as the benefits of control policies for regulating the precursors of acid deposition. The damage estimates contained in the 1985 Assessment assume fairly pristine environmental conditions which are not necessarily consistent with economic efficiency objectives. In general, information about the incremental benefits of various control options must be integrated with information about incremental control costs to determine economically efficient levels of damage reduction.

Second, the 1985 Assessment was regional rather than national in its geographic scope. The information necessary to conduct a national-level assessment is not yet available. Given this limitation, the regional focus of the 1985 Assessment was directed largely toward the Eastern half of the United States, where monitored deposition levels are higher, on average, than in other parts of the country and where research on the physical effects of acid deposition has been concentrated. Four types of receptor systems, potentially sensitive to gaseous air pollutants and acid deposition, were included in NAPAP's economic analysis.

These were crops, forests, aquatics, and materials. These areas were selected based on scientific and public concern about the possible physical effects of acid deposition [1]. For consistency with economic methods and data bases only the following areas were subjected to analysis: commercial agriculture; commercial forests; recreational fishing; and common building, cultural and infrastructure materials. The remainder of this paper focuses specifically on the research performed to estimate the potential economic impacts of air pollution in the eastern U.S. on timber and selected primary wood product markets in the nation as a whole.

1.2. Evidence of Growth Slowdowns in the Eastern U.S.

Recent studies have reported both localized and region-scale decreases in the growth rates of several commercially-important forest species in the eastern U.S. Red spruce decline in high elevation was first reported by Siccama et al. [2] in the Green Mountains of Vermont. Evidence included a decrease in the basal area growth rate and density of 50% between 1965 and 1980 and the presence of visible symptoms such as needle loss. Reduced growth was found in all observed age classes. Similar evidence of red spruce decline, including increased mortality, has been observed in other areas of the high elevation northeastern and southeastern forests [3] with the symptoms seeming to increase with elevation. The association between growth slowdowns and high elevation is important because air pollution concentrations and deposition tend to increase with elevation. In addition to the studies of growth slowdowns in high elevation forests, growth slowdowns have been detected in low elevation forests [4]. However, the conclusions in this study are based on changes in tree ring growth, which is generally regarded as less certain than the visible symptoms observed in high elevation spruce.

Another source of evidence that Eastern forests may be experiencing a reduction in growth rates is the periodic analysis of timber inventories in the Southeastern United Sates conducted by the Forest Service's Southeastern Forest Experiment Station (FIA analysis). The most recent FIA analysis indicates that the annual growth rates of softwood timber have declined over a fairly large geographic area compared to the previous FIA analysis [5]. For example, the radial growth of yellow pines in the Piedmont Region and mountains of Georgia was 20-30% less between 1972 and 1982 than between 1961 and 1972. Further investigations indicate that radial growth rates of most yellow pines under 16 inches in diameter declined by between 30 and 50% throughout the Piedmont, Mountain, and Coast Plain Regions of the Southeast.

A number of causes have been proposed for the growth rate reductions in the Southeast. In addition to air pollution, these causes include: 1) aging of stands, 2) increased stand density, 3) increased hardwood competition, 4) drought, 5) diseases, and 6) changes in land use. It is not possible, at present, to determine which of the above potential effects might have caused the changes in growth rates. The hypothesis that acid deposition, one of several candidates, caused the growth slowdowns cannot be accepted or rejected with present scientific information. For that reason, we do not attempt to link our analysis to acid deposition. Our model and analysis is are general; the changes in growth rates are hypothetical and could be due to any cause. However, the results presented in Section 4 are based on growth reductions that are consistent with those reported by the U.S. Forest Service [5].

In view of the inconclusive nature of the information about the physical effects of acid deposition, it would be wrong to assume that one can accurately project the effects of acid deposition or acid deposition controls on stumpage and forest product markets in the United States. However, it would also be incorrect to assume that economic analysis of acid deposition damages has nothing to contribute to acid deposition-related research at this time. Specifically, the research presented in this paper can serve as a basis for characterizing the potential scope of the economic impacts of acid deposition and for assessing the sensitivity of the simulated economic impacts of acid deposition to different assumptions about the nature of the potential physical effects of acid deposition on tree growth. Under no circumstances should the results presented in this paper be viewed as forecasts about the future economic impacts of acid deposition.

1.3. Valuing Damages

Two different approaches can be used to evaluate the economic damages of air pollution-induced decreases in forest growth [6]. The first is the so-called damage function approach. This technique uses dose-response functions to translate changes in air pollution levels into physical damages. Physical damages are then multiplied by a unit economic value, such as a market price, to obtain a measure of economic damages.

For example, if the effects of acid deposition on the annual growth increments for different size trees of a particular species in a given location were known, the impact of this effect on the total inventory volume for that species could be calculated on an annual basis. The projected annual change in the inventory could then be multiplied by a projected stumpage price for each year of the projected life of the current inventory to obtain annual estimates of the future damages of acid deposition to the subject species. Discounting these values at an appropriate measure for the opportunity cost of capital and then summing these values for each year in the projection period would provide a measure of the present value of the damages caused by acid deposition to the species in question. Repeating these steps for all commercially-important species on all acres of commercial timberland would result in an estimate of the present value of the aggregate damages of current levels of acid deposition in commercial timberland.

These are several shortcomings associated with applying the above approach, or variants of it, to measure the economic value of the damages caused by current levels of acid deposition or other air pollutants. For example, the damage function approach can sometimes be used to approximate the economic losses of producers of goods and services and, in some cases, the economic damages suffered by owners of natural resources, such as timberland. However, this approach does not capture the effects which acid deposition may have, indirectly, on firms which process stumpage into lumber, plywood, paper and a large number of other products or on the consumers who purchase goods and services that contain wood products. A second problem is that it ignores substitutions which individuals and firms can make in their consumption and production decisions due to changes in prices. Generally speaking, extremely unrealistic assumptions have to be made about the preferences of individuals, the technology of firms, and the structure of the markets being analyzed for the damage function approach to yield damage measures which are consistent with economic theory.

A second approach overcomes these shortcomings by using mathematical representations (models) of supply and demand curves in appropriate markets to characterize the behavior of consumers and producers. Information about the direction and magnitude of environmental impacts is generally used in conjunction with this approach to shift the relevant supply or demand curves in affected markets to simulate the behavioral responses of consumers and producers. Appropriate damage measures can then be evaluated from these simulated shifts in supply and demand curves. This approach is illustrated in Figure 1, which characterizes price (P) and output (Q) determination in a market for stumpage, given market demand and supply curves D, S for stumpage. The wel fare of consumers (e.g. buyers of stumpage) can be approximated [7] by the

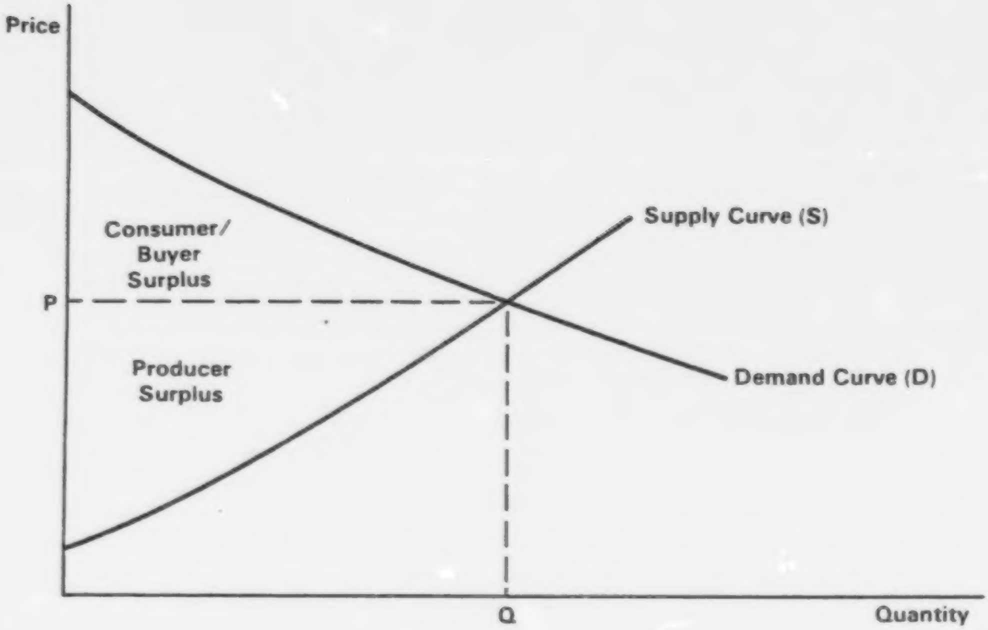

FIGURE 1
Price and output determination in a stumpage market.

area underneath the market demand curve and above the price line, drawn horizontal from P. This area, known as consumer or buyer surplus, is equal to the maximum amount individuals are willing to pay for a single unit of stumpage less the amount actually paid. Producer surplus measures the welfare of timber owners in the market (e.g. producers of stumpage). It is given by the area above the market supply curve and below the price line. This area is equal to the difference between the amount received by timber owners from the sale of stumpage less the minimum cost of producing Q units of stumpage. Total surplus in the market is approximated by the sum of these two areas.

Figure 2 shows how information about market supply and demand curves can be used to value economic damages due to acid deposition. The physical affects of acid deposition are shown here by the inward shift of the market supply curve for stumpage from S to S'. This type of effect is consistent with the movement of the market supply curve for a commercial stumpage in response to reduced yields. This change results in a higher market price (P') and reduced output (Q'). The reduction in total surplus in the stumpage market is approximated by the shaded area between the two supply curves and represents the measure used to value the damages of reduced tree growth on buyers and sellers in commercial stumpage markets. A similar type of analysis can be performed in forward markets to determine damages to the consumers of the forward products of stumpage such as lumber and plywood.

2. TECHNICAL APPROACH

The economic effects of hypothetical reductions in tree growth were simulated using modified versions of the softwood and hardwood forest sector models, TAMMSOFT [8] [9] and TAMMHARD [10], and a forest inventory projection model, TRAS [11] [12], to which the economic models are physically linked. A brief description of these models and a discussion of how they were used to assess the economic impacts of reduced tree growth follows.

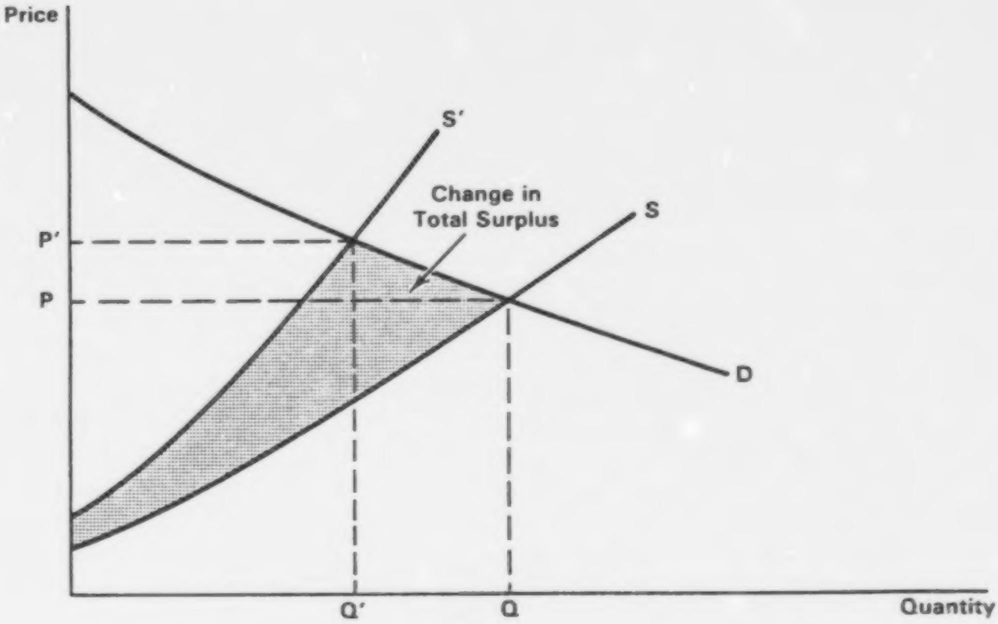

FIGURE 2
Measurement of economic damages due to acid deposition.

2.1. Models

The basic function of TRAS is to provide the TAMM models with information about the size of the growing stock inventory of trees which is potentially available for harvesting within each region. TRAS represents regional inventories as aggregate per-acre stands of trees, broken down by two species groups (hardwoods and softwoods) and two ownership groups (forest industry and nonindustrial private). The trees in each of the four representative stands are further divided into eleven two-inch diameter classes. Given user-specified values for annual radial growth and natural mortality in each of these classes and for the number of new trees in the smallest diameter classes, TRAS calculates the annual change in the number of trees in each diameter class. TRAS does this by first estimating the potential increase in the number of trees within each diameter class in the absence of natural mortality and harvesting. Annual net growth is then calculated for each class by subtracting natural mortality. Harvest levels are calculated by the TAMM models for each species and owner group in each region. TRAS allocates these removals to different diameter classes and subtracts them from the remaining inventory of trees to determine the annual change in the number of trees in each diameter class. This change is used in conjunction with the beginning inventory of trees to update the inventory of trees in each diameter class. TRAS then repeats this cycle on an annual basis to maintain the proper accounting balance within the regional inventory.

TAMMSOFT and TAMMHARD are multi-market, spatial equilibrium models of the softwood and hardwood stumpage and primary forest products industries in the United States. TAMMSOFT contains six domestic demand regions in which final products are consumed and eight domestic supply regions in which timber is harvested and three wood products-lumber, plywood, and pulp-are produced. TAMMHARD contains one national consuming region and four domestic supply regions in which stumpage is harvested and lumber and pulp are produced. Physical linkages between the hardwood and softwood models are accomplished through a common pulpwood supply sector physically located in TAMMSOFT. The method of linking the two models is unique to this assessment and is discussed in detail in Callaway et al. [13].

In both models each region has either demand or supply equations, as appropriate, for lumber and plywood. Product and stumpage markets in each region are linked together. The regional supply equations for each final product are specified so that the amount of each product supplied in a region is sensitive to changes in both the final product price and the price of softwood and hardwood stumpage. Aggregate stumpage demand is derived directly from product supply by a series of conversion factors. The conversion factors can be adjusted to reflect the effects of technological change on the efficiency of processing lumber and plywood. The stumpage supply equations in each of the producing regions in the models reflect the harvest response of forest industry and nonindustrial private owners to changes in stumpage prices and inventories. The latter information is supplied to both models directly from TRAS. Finally, a spatial equilibrium solution is calculated in both stumpage and product markets within the models for each year in the projection period 1976-2030.

TAMMSOFT also contains a Canadian supply region in which lumber is produced for export to the United States. Total Canadian softwood lumber production is modeled as a function of producer's profit margin, which is the difference between the softwood lumber price and the sum of delivered wood costs and lumber manufacturing costs. Delivered wood costs are related functionally in each period to Canadian softwood lumber production in the previous period and a time trend. Canadian domestic demand for lumber and lumber exports to countries other than the United States are determined exogenously, which prevented the computation of effects on Canadian consumers of changes in lumber prices. The Canadian stumpage sector also is not modeled explicitly in TAMMSOFT. Canadian softwood lumber production, softwood lumber exports to the United States, and Canadian softwood lumber price are all determined endogenously as a part of the spatial equilibrium solution generated by the linked system of models.

The system of models described above produces annual information about the size, species and ownership composition of the growing stock inventory of trees on commercial timberland in each region. It also provides information on an annual basis about regional stumpage prices and harvest levels, regional commodity prices, output levels, and consumption in lumber and plywood markets. Finally, the TAMM models were modified for this study to provide welfare measures of consumer and producer surplus that are theoretically consistent with a spatial equilibrium in a vertically integrated market chain [14] [15]. For this study, total welfare changes due to hypothetical reductions in tree growth were represented by changes in the sum of: 1) consumer surplus of the buyers of lumber and plywood, 2) producer surplus of the producers of lumber and plywood, and 3) the producer surplus of timberland owners.

2.2. Methods

Two sets of simulations were performed. The first set of simulations was conducted to examine the effects of hypothetical changes in tree growth rates in the Eastern United States on growing stock inventories, stumpage and primary products markets, and the welfare of buyers and sellers in these markets in the United States. This set of simulations assumes that air pollutants generated either in Canada or in the United States do not damage Canadian forests. For the second set of simulations it was assumed that Canadian forests would be damaged by air pollution generated in the United States or Canada. These simulations explore the effects of reduced tree growth in both the United States and Canada on the export trade between the two countries and on the welfare of Canadian lumber producers. The methods used in connection with both sets of simulations are described below.

First, base case values for appropriate economic impact variables and welfare measures were established by running the system of models for the period 1985-2030. Base case assumptions regarding key driver variables in TAMM and TRAS are, for the most part, identical to those used by the U.S. Forest Service [16] and reported by Haynes and Adams [9]. Major assumptions include: 1) future housing starts at 1.7 million units in 1990, 1.9 million units in 2000, and 1.5 million units in 2030; 2) a 10% increase in the efficiency of processing lumber and plywood during the projection period; and 3) 319 million acres of commercial timberland remaining in 2030. The initial inventories contained in TRAS, as well as the radial growth rates of timber used in the base case, are also identical to the growth rates used by the U.S. Forest Service [16].

The second step of the analysis involved adjusting relevant parameters within the TAMM and TRAS models to simulate reduced tree growth. For the first set of simulations, hypothetical reductions in tree growth were simulated by reducing the radial growth rates that are used by TRAS to calculate the annual net growth of trees from one diameter class to the next for both hardwoods and softwoods. Since data to provide appropriate guidance about the magnitude and distribution of recently-observed growth slowdowns by species and by diameter class are not yet well developed, uniform growth rates changes across species and all diameter classes were assumed. Accordingly, the annual radial growth rates in TRAS were uniformly reduced in the Northeast and Southeast timber supply regions* by 10,15, and 20%. These growth rate reductions are generally smaller in magnitude than those reported by Sheffield et al. [5] for several pine species in the southeastern United States. However, there is considerable speculation that perhaps as much as a half of the observed change in radial growth among softwoods in the southeast can be explained by natural phenomena, such as increased stand density and increasing competition with hardwoods. If that is the case, then the radial growth rate changes used in this analysis may represent a realistic, but nevertheless hypothetical, range of air pollution effects.

Simulating reduced tree growth in Canadian forests is complicated by several factors. First, very little is known about the effects of long-range pollution on Canadian forests. Second, the response of public timberland owners in Canada (who own the majority of Canadian timberland) to reduced forest growth is difficult to predict. Finally, and in a more practical vein, the Canadian stumpage sector is not modeled explicitly in TAMM. In spite of these problems, we believe that characterizing the effects of reduced forest growth in both the U.S. and Canada on the timber trade between the two nations, if only on a preliminary basis, represents a worthwhile policy exercise. In keeping with that belief, we simulated the effects of reduced tree growth in Canada and the U.S. by increasing the intercept in the Canadian delivered wood cost functions in TAMMSOFT by $1.00, $2.00 and $3.00 (U.S. 1967) for each of the three reduced growth cases in the U.S. These adjustments have the effect of shifting the Canadian lumber supply curve inward in each year. This is consistent with the effects of an increase in the price of Canadian stumpage which could be the result of either air pollution-induced market adjustments or market-oriented public policies.

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* The Northeast includes Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, Pennsylvania, Rhode Island, Vermont, and West Virginia; the Southeast includes Florida, Georgia, North Carolina, South Carolina, and Virginia.

In the third step of the analysis, the system of models was rerun for the period 1985 to 2030 for each of the reduced growth cases identified above. All other driver variables were left unchanged from the base case. The resulting values for appropriate economic impact variables were recorded and the difference between the base case values and the values obtained using the revised tree growth rates were attributed to the effects of a particular reduction in tree growth. Finally, the annual value of the economic damages for each reduced growth case was calculated as the difference between the net present value of total estimated welfare for the period 1985-2030 with and without the growth rate change. The total damage estimate for each reduced growth case was annualized (i.e., levelized) using a 10% real discount rate.

3. RESULTS

This section presents the results of the simulations described in Section 2. Sections 3.1 to 3.4 focus on the effects of simulated reductions in tree growth rates in the eastern United States (only) on growing stock inventories, prices, and output levels in both stumpage and lumber markets and on the welfare of buyers and sellers in these markets. Finally, Section 3.5 covers the effects of simulated reductions in tree growth in Canada and the United States on the lumber trade between Canada and the United States.

3.1. Impacts On Growing Stock Inventories

Table 1 compares the TAMM Base Case projections of combined softwood and hardwood growing stock inventories in the year 2030 with the inventory projections associated with simulated reductions in tree growth rates of 10, 15 and 20%. Three aspects of the simulated effects of reduced timber growth on commercial timber inventories deserve attention. First, the projected decrease in the Southeast timber inventory in all three reduced growth cases is approximately twice as great as the projected decrease in the Northeast inventory. This is due to the composition of the growing stock inventory in the Southeast, which contains a relatively larger share of young, fast growing trees than the Northeast. Reducing the growth rates of these trees causes a larger and longer lasting decrease in total inventory volume than does reducing the growth rates of older, slower growing trees. Second, reducing tree growth rates in the Northeast and Southeast causes timber inventories in other supply regions to decrease by roughly 3.5 to 10.0% depending on the magnitude of the timber

TABLE 1
Percentage Changes in Combined Softwood and Hardwood Growing Stock Inventories Due to Simulated Reductions in Radial Growth in the Northeast and Southeast: 2030 Forecasts.

Region	Base Case (Billion Cubic Feet)	Growth Rates in the Northeast and Southeast Reduced by 10%, 15%, and 20% (Percentage Change from Base)		
		10%	15%	20%
Northeast	112.48	-8.63	-13.47	-19.09
Southeast	125.11	-20.54	-29.21	-38.28
Other Supply Regions	239.26	-3.45	-6.05	-10.08
Total U.S.(a)	476.85	-9.16	-13.88	-19.60

(a) Includes only the lower 48 states.

growth rate reductions in the two eastern regions. This is an induced effect of reduced tree growth in the eastern U.S., which leads to an improvement in the comparative cost advantage of other supply regions in the interregional trade for lumber and plywood. The improved competitive position of these regions (relative to the two eastern regions) leads to higher lumber and plywood production, larger harvest levels and smaller inventory volumes than in the Base Case.

Third, the direct and induced effects of reduced tree growth rates on projected timber inventories for the U.S. as a whole range from about 10 to 20%, depending on the case selected. One way to place these effects in perspective is to compare these inventory changes with those due to insect pests and disease. Callaway et al. [13] have estimated that the physical effects of a 15% growth reduction of timber in the Northeast and Southeast are roughly comparable to the physical damage caused by insect pests and disease on all eastern commercial timberland.

3.2. Impacts On Stumpage Markets

Table 2 shows the effects of simulated reductions in timber growth rates on the combined softwood and hardwood harvest levels projected by TAMM for the year 2030. As expected, the size of the combined softwood and hardwood harvest for the U.S. as a whole decreases from the Base Case levels as the magnitude of the simulated timber growth rate reduction is increased. The percentage decreases in the combined harvest are small (i.e., less than 1.5% in the most severe reduced growth case) because smaller harvests in the Northeast and Southeast are offset somewhat by larger harvests in the other supply regions. Projected stumpage prices for 2030 (not shown) are higher in all regions when timber growth rates were increased in the two eastern regions. For example, projected softwood stumpage prices range from 4 to 9% above Base Case levels in the Northeast and 12 to 25% higher than Base Case levels in the Southeast. In the Pacific Northwest, which is an important competitor in softwood lumber and plywood markets, softwood stumpage prices are from 14 to 25% higher than Base Case values, depending on the severity of the growth reduction.

To understand these results a distinction should be made between stumpage price increases in regions directly affected by growth reductions and price increases in other regions. In the first case, stumpage price increases are accompanied

TABLE 2
Percentage Changes in Combined Softwood and Hardwood Harvests Due to Simulated Reduction in Radial Growth in the Northeast and Southeast: 2030 Projections.

Region	Base Case (Billion Cubic Feet)	Growth Rates in the Northeast and Southeast Reduced by 10%, 15%, and 20% (Percentage Change from Base) 10%	15%	20%
Northeast	3.09	-3.24	-4.53	-6.15
Southeast	5.02	-6.22	-11.16	-14.81
Other Supply Regions	13.42	1.94	3.72	4.62
Total U.S.(a)	21.53	-0.71	-0.93	-1.46

(a) Includes lower 48 states for softwood and Eastern U.S. only for hardwood.

by smaller harvests. As the productivity of growing stock inventories in regions directly affected by growth reductions declines, harvestable stumpage becomes more scarce. In response to this increased scarcity, timberland owners are willing to sell stumpage only if they receive higher prices. These higher prices, however, increase the costs of producing lumber and plywood, so manufacturers of these products reduce both their output levels and their purchases of inputs, i.e., stumpage. The net effect is to increase stumpage prices and reduce harvest levels in those regions directly affected by reduced growth.

In regions where timber growth remains unchanged, both stumpage prices and harvest levels increase. Even though manufacturers of lumber and plywood in regions directly affected by growth reductions reduce their output, they still must sell their products at higher prices if they are to recover the higher production costs caused by higher stumpage prices. Higher product prices in the two eastern regions increase the competitiveness of lumber and plywood produced in other regions where growth rates remain unchanged. Manufacturers of these products in other regions, therefore, increase both their output levels and their purchases of stumpage inputs. As a result, stumpage prices and harvest levels in other regions rise.

3.3. Impacts On Product Markets

Table 3 shows the impacts of simulated reductions in timber growth rates on projected production of hardwood and softwood lumber (combined) in the U.S. and on imports of Canadian softwood lumber for the year 2030. The same general patterns that were present in domestic stumpage markets are also observed for this one, but representative, product market. That is: projected production levels in the Northeast and Southeast are lower than in the Base Case, while lumber production in other regions is slightly higher than in the Base Case. The net result is a decrease in domestic lumber production ranging from about 3 to 7%, depending on the magnitude of the growth reduction. There is, however, a substantial increase in imports of Canadian softwood lumber which partially offsets this decrease: even in the "worst" case the total of U.S. lumber production plus Canadian imports is less than 3.5% below the Base Case level.

TABLE 3
Percentage Changes in Combined Softwood and Hardwood Lumber Supplies Due to Simulated Reductions in Radial Growth in the Northeast and Southeast: 2030 Projections.

Source of Combined Lumber Supply by Region	Base Case (Billion Board Feet)	Growth Rates in the Northeast and Southeast Reduced by 10%, 15%, and 20% (Percentage Change from Base)		
		10%	15%	20%
Northeast(a)	3.41	-1.76	-2.93	-4.40
Southeast	12.17	-21.53	-29.74	-35.91
Other Supply Regions	36.48	2.88	3.07	2.08
Total U.S.(b)	52.06	-3.13	-4.99	-7.22
Imports of Canadian Softwood Lumber	9.62	8.21	12.27	16.84

(a) Softwood lumber supplies in the Northeast are price inelastic in TAMM.
(b) Includes lower 48 states for softwood and Eastern U.S. only for hardwood.

In view of the vertical linkages which exist between stumpage and wood product markets and the horizontal trade linkages between regions in both plywood and lumber markets, these results are not so surprising. As previously mentioned, simulated reductions in tree growth rates in the eastern U.S. confer a comparative cost advantage on lumber and plywood producers in other supply regions. As a result, regions directly affected by these growth reductions reduce lumber and plywood production and either import a larger, or export a smaller, quantity of wood products in each period. Producers in other supply regions tend to increase their output of lumber and plywood either to increase their exports to, or reduce the volume of imports from, those regions directly affected by the simulated reductions in tree growth rates. Since increased production causes the demand for stumpage to increase in other supply regions, input costs and product prices in these regions also rise until a new trade equilibrium is established.

A similar process occurs at the international level. As prices of wood products in the U.S. rise, the nation exports fewer and imports more wood products. This pattern is reflected primarily in the growth of Canadian imports of lumber into the U.S. By distributing the impacts of timber growth reductions in one or two regions over a broader geographical area and a larger number of producers, these changes in domestic and international trading patterns tend to cushion the decreases in total U.S. output of wood products which might otherwise occur.

3.4. Welfare Impacts

Table 4 gives estimates of the effects of simulated reductions in tree growth on the economic surplus of timber owners, lumber and plywood producers and the buyers (consumers) of these products. As previously stated, these estimates represent changes from Base Case values in the annualized net present value of each of the relevant economic surpluses, cumulated over the period 1985 to 2030. In aggregate terms, these estimates reflect the value of the economic damages which can be attributed to the simulated timber growth rate reductions over the period. These damages, shown in the last row of Table 4, ranged from about $340 to $510 million annually, depending on the severity of the hypothetical growth reduction. These damages are always small in comparison to the Base Case--always less than 1.0% of the roughly $70 billion total surplus estimate. The corresponding changes in the net present value of damages over the entire period (not shown) are roughly $3.4, $4.4 and $5.0 billion.

The distributional impacts of the assumed growth reductions are shown in the first three rows of Table 4. In general, timber owners as a group benefit from reductions in radial growth due to their ability to pass along higher prices to

TABLE 4

Estimated Changes in the Annualized Economic Surplus of Timber Owners, Lumber and Plywood Producers and Consumers Due to Simulated Reductions in Radial Growth in the Northeast and Southeast (millions of 1984 dollars).

Economic Group	Base Case Surplus	Growth Rates in the Northeast and Southeast Reduced by: 10%	15%	20%
Timber Owners	5,603.8	63.4	109.9	220.7
Producers	23,887.6	-63.4	-40.4	148.0
Consumers	40,178.2	-342.4	-516.3	-878.8
Total	69,669.6	-342.4	-446.8	-510.1

the producers of primary wood products. The annualized benefit received by timber owners was estimated to range from about $60 to $220 million. The picture for producers of primary wood products is mixed. As a group, they experience annual damages in the 10 and 15% reduced growth cases of $60 and $50 million but receive roughly $150 million in annual benefits when radial growth is reduced by 20%. Of the three groups, consumers of wood products bear the brunt of the damages due to simulated reductions in radial growth. The decreases in economic surplus of this group ranged from about $340 to $880 million annually. Moreover, a substantial portion of these losses represent transfers of economic surplus from consumers to producers and timber owners as physical damage levels were increased.

Table 4 does not present a geographic breakdown of economic damages. However, timber owners in the southeast suffer economic damages due to all growth slowdowns. In addition, producers in that region are hurt considerably more by these changes in growth than producers in the Northeast, who actually experience slight benefits. This suggests a relative (but not absolute) improvement in the competitive position of the Northeast over the Southeast due to decreased tree growth in both regions.

3.5. Impacts on Canadian Lumber Trade

Previously, in Table 3, we saw that Canadian exports of softwood lumber to the U.S. in 2030 increased with the severity of simulated forest damage in the eastern U.S. We now examine how robust this result is in the face of simulated increases in the delivered cost of softwood to Canadian lumber producers.

Table 5 shows how average annual exports respond to simulated decreases in radial growth in the eastern U.S. and to simulated increases in Canadian delivered wood costs during the period 1985-2030. Holding the change in Canadian delivered wood costs constant at four specified levels (i.e., $0.00, $1.00, $2.00 and $3.00), we can read down each column to see how Canadian lumber exports to the U.S. respond to simulated forest damage in the eastern U.S. In all four cases involving changes in Canadian delivered wood costs, the volume of average annual softwood lumber exports to the U.S. increases with the magnitude of the growth reduction in the U.S. However, when the change in radial growth in the eastern U.S. is held constant, one can see by reading across each row that this pattern is reversed. In all but two cases, an increase in Canadian delivered softwood costs results in a decrease in the volume of average annual softwood lumber exports to the U.S.

TABLE 5
Effects of simulated reductions in radial growth in the Eastern U.S. and simulated increases in Canadian delivered wood costs on average annual exports of Canadian softwood lumber to the U.S. 1985-2030 (billion board feet).

Growth Rate Change--U.S. (pct. decrease)	Increase in Canadian Delivered Softwood Costs (1967 U.S. Dollars)			
	Base	$1.00	$2.00	$3.00
Base	10.70	10.57	10.41	10.24
10	11.10	10.87	10.57	10.54
15	11.24	10.97	10.51	10.80
20	11.68	11.03	10.60	10.89

Figure 3 illustrates how air pollution-induced increases in U.S. and Canadian stumpage prices influence exports of Canadian softwood lumber to the U.S. using a simple two-region trade model. Initially, we assume no air pollution damage to either U.S. or Canadian forests. Under this assumption, S_0 units of lumber are produced in Canada at a price of P_0. Canadian lumber consumption is fixed at D (as is the case in TAMM), so that Canadian lumber exports to the U.S. are equal to S_0-D.

If we now assume that air pollution damages U.S. forests (only), then the resulting increase in U.S. stumpage prices would cause the U.S. lumber supply curve in Figure 3 to shift inward. This leads to an increase in the U.S. demand for Canadian lumber at the new market price P_1. Canadian lumber production increases accordingly to S_1 and, now, S_1-D units of lumber are exported from Canada to the U.S. Note that, in the process, the producer surplus of Canadian lumber producers increases by an amount equal to the area between P_1 and P_0 above the initial Canadian supply curve.

If we assume that acid deposition also damages Canadian forests, the subsequent increase in Canadian stumpage prices would induce an inward shift in the Canadian lumber supply curve, as shown in Figure 3. This chain of events leads to an increase in the trade price of lumber from P_1 to P_2 and a decrease in Canadian lumber production from S_1 to S_2. Canadian lumber exports to the U.S. also fall by the same amount. Note, however, that lumber exports as depicted in Figure 3 are still greater than they were in the initial case, when forests in both countries were experiencing no air pollution damage. But this result is just one of two possible outcomes. Had the Canadian lumber supply curve in Figure 3 been shifted further inward, both Canadian lumber production and lumber exports to the U.S. would have fallen below initial levels indicated by

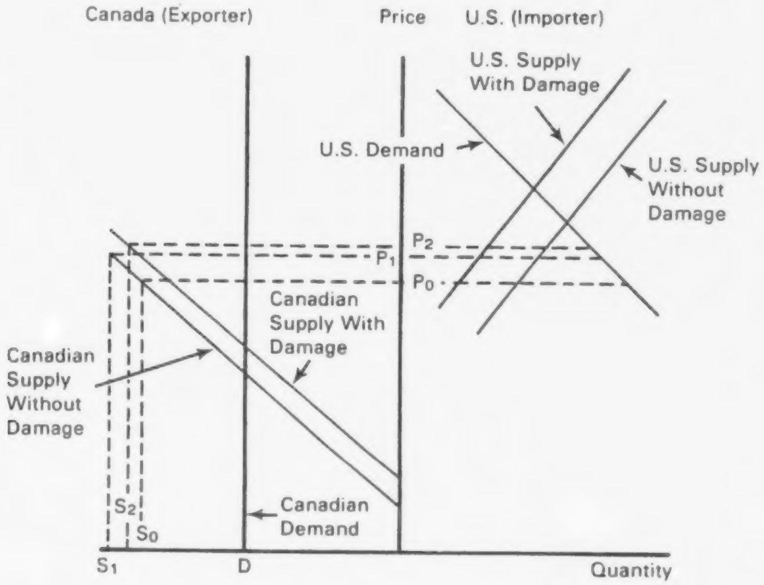

FIGURE 3
Effects of air pollution-induced stumpage price increases in the U.S. and Canada on U.S.-Canadian softwood lumber trade.

S_0. Thus, the eventual effect of air pollution on Canadian lumber production and exports to the U.S. depends: 1) on the relative movement of the two supply curves as a result of increased stumpage prices and 2) on the curvature of the lumber supply and demand curves in both regions in the neighborhood of the price-quantity changes which take place.

The effect of joint increases in stumpage prices in both regions on the producer surplus of Canadian lumber producers is also difficult to determine on a priori grounds. This is because there are basically two counteracting forces at work. Increases in Canadian stumpage prices lead to higher wood costs and lower profits. However, higher trade prices lead to increased revenues and higher profits. The net effect of these two forces on the producer surplus of Canadian lumber producers depends on the same two factors which influence changes in the volume Canadian lumber production and lumber exports to the U.S.

Table 6 shows how the annualized value of the producer surplus of Canadian softwood lumber producers responds to simulated forest damage in the Eastern U.S. and to increases in Canadian delivered softwood costs. Consistent with the previous discussion, it can be seen that, when the change in delivered wood cost is held constant, the annualized producer surplus of Canadian lumber producers generally increases. This result does not appear to hold at the highest damage level where higher lumber profits in the U.S. trigger increased domestic lumber production capacity within TAMM.

One reason why these damages are not greater is that simulated reductions in tree growth rates in the eastern U.S. allowed lumber and plywood in other regions, including Canada, to become more competitive with eastern producers. As a result, economic activity in both stumpage and primary wood product markets in these other regions increased and thus buffered the adverse effects of reduced timber growth in the nation as a whole. This general pattern was not affected by increases in the intensity of simulated timber growth reductions.

Table 6 also shows that the welfare of Canadian softwood lumber producers, as measured by changes in producer surplus, generally decreases in response to increases in Canadian delivered softwood costs. As we pointed out earlier, this is due to the fact that increases in delivered wood costs cause softwood lumber production costs to rise more rapidly than the increase in lumber revenues due to higher trade prices. On balance, the results from Table 6 suggest that as long as increases in Canadian stumpage prices due to air pollution damages are not too great, Canadian lumber producers may actually benefit from air pollution damages in the U.S. and earn higher profits than under pristine environmental conditions. Although the effect of increased prices on the

TABLE 6

Effects of simulated reductions in radial growth in the Eastern U.S. and simulated increases in Canadian delivered wood costs on the value of the annualized producer surplus of Canadian lumber producers (millions of 1984 dollars)

Growth Rate Change--U.S. (pct. decrease)	Increase in Canadian Delivered Softwood Costs (1967 U.S. Dollars)			
	Base	$1.00	$2.00	$3.00
Base	1166.9	1141.6	1116.3	1087.3
10	1195.3	1175.2	1146.3	1126.4
15	1255.1	1241.0	1228.5	1192.5
20	1250.4	1196.9	1143.4	1175.8

welfare of Canadian consumers is unambiguously negative, no computations could be done of the size of the effect.

4. SUMMARY

In this paper we described the framework which was developed for the 1985 Damage Assessment to assess the economic impacts of air pollution-induced decreases in forest growth in the eastern United States. The evidence for concern about the potential effects of air pollution and, more specifically, acid deposition on forest growth was presented. The fact that recently observed decreases in tree growth rates in the eastern United States cannot be linked scientifically to increases in acid deposition was stressed. Therefore, the results of this study should not be viewed as forecasts of the economic consequences of increases in acid deposition. Rather the results are intended to characterize the potential scope of the economic impacts of acid deposition and to test the sensitivity of these impacts to different assumptions about the intensity of the potential physical effects of acid deposition on tree growth.

We estimated the effects of hypothetical reductions in tree growth rates in the eastern United States of 10, 15 and 20% on growing stock inventories, stumpage and primary wood product markets and on the economic welfare of buyers and sellers in these markets. The estimated annual damages due to hypothetical reductions in tree growth for the period 1985-2030 ranged from approximately $340 to $500 million, depending on the severity of the simulated growth reduction. These damages represent a small (less than 1%) fraction of the combined annual economic surplus of timber owners and the producers and is that simulated reductions in tree growth rates in the eastern United States allowed lumber and plywood producers in other regions, including Canada, to become more competitive with eastern producers. As a result, economic activity in both stumpage and primary wood product markets in these other regions increased and thus buffered the adverse effects of reduced timber growth in the nation as a whole. This general pattern was not affected by increases in the intensity of simulated timber growth reductions.

We also looked at the responsiveness of Canadian softwood lumber exports and the producer surplus of Canadian softwood lumber producers to simulated forest damage both in the U.S. and Canada. Generally speaking, we found that softwood lumber exports to the U.S. increased with the severity of simulated forest damage in the U.S., but decreased in response to simulated increases in Canadian delivered wood costs. The producer surplus of Canadian softwood lumber producers generally followed the same pattern. Overall, the results of this analysis suggest that, as long as Canadian forest damages are not too severe, Canadian producers may well be the beneficiaries of air pollution damages and could earn higher profits than under pristine environmental conditions. Comparable calculations could not be done for Canadian consumers or timber owners.

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SOME ECONOMICS OF THE GRAND CANAL

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SOME ECONOMICS OF THE GRAND CANAL

1. Introduction

In recent years the popular press has paid considerable attention to the GRAND Canal scheme advocated by Kierans (1985) and others. The scheme calls for the conversion of all or part of James Bay into a freshwater lake which would accumulate run-off from northern rivers in Ontario and Quebec. The water would be pumped south to the Great Lakes via the Harricanaw, Ottawa, and French Rivers from whence it could be diverted at several points to augment water supplies in the United States. A combination of inflows from the north and outflows to the south would permit stabilization of water levels in the Great Lakes, particularly Lakes Huron and Michigan. The water exported to the United States would supplement scarce regional supplies for urban and agricultural use.

The plan has been unfavourably received in many quarters. Newspaper reports and editorials (e.g. Toronto Star, 23 May 1985, Globe and Mail, 3 Jan 1985) have stressed potential environmental and political costs. The Inquiry on Federal Water Policy (The Pearse Inquiry) devoted a chapter to Water Exports and concluded that the federal government should resist pressures to support any large scale international diversion scheme, at least until the Cabinet has determined under what conditions, if any, major water export schemes might be approved and until legislation is in place to conduct thorough assessments of all proposals and to license the water exports (Chapter 12). The Minister of the Environment has declared that, at present, he is opposed in principle to the project (MacMillan, 1986).

Nevertheless, the scheme has attracted serious attention both in the public and private sectors. Premier Bourassa (1985) of Quebec strongly promoted studies of the concept in his book published shortly before his election. Four large Canadian engineering firms, SNC and Rousseau, Sauve and Warren of Montreal, Bechtel Canada, and the UMA group of Calgary have formed a joint venture with the GRAND Canal Co. of St. John's to carry out engineering and other studies of the scheme. This group has applied for $763,000 through the National Research Council (NRC) and the Department of Supply and Services to fund the major portion of the cost of preparing a "project statement" which would form the basis of subsequent proposals for private and public funding. Despite the strong opposition of much of the federal bureaucracy, NRC seems committed to providing financial assistance to the GRAND Canal Company.[1] NRC's argument seems to be that the proposal is a far-sighted one with potential merit and that federal funds should be provided to help the GRAND Canal Co. better understand both the costs and benefits of the project.

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[1] Letter from Keith Glegg, Vice-President Technology Transfer, National Research Council, to Hon. Charles Caccia, 13 January 1986.

We are thus faced with a proposal which is regularly dismissed out of hand by most federal authorities, yet which persists on the policy agenda. Further pursuit of the proposal is likely to involve substantial expenditures of public and private funds which, given current fiscal restraint, should be carefully husbanded. Accordingly, it seems useful to attempt to lay out some basic issues surrounding the proposal in the hope of directing public discussion towards the central issues in dispute.

Following the suggestion of Scott (1985), the discussion will be organized in the economic framework of Cost-Benefit Analysis. In a paper prepared for the Inquiry on Federal Water Policy, Scott argued vigorously that this approach provides a systematic procedure for ensuring that water development proposals are shaped so as to provide the maximum net advantage to the country. A definitive cost-benefit analysis is, of course, out of the question in the absence of much more detailed information about the project. Nevertheless, the discipline involved in formulating the problem in terms of costs and benefits aids in deciding whether the project is at all viable and, if so, in identifying the areas in which detailed information is most urgently required.

The next section of the paper presents the case made by the proponents of the GRAND Canal project and the major objections which have been raised against it. The following section examines more systematically the costs and benefits associated with the project. Where information is available, an attempt is made to develop rough estimates of their magnitude. A number of fallacies to avoid in estimating benefits are discussed. A final section summarizes and concludes the paper.

2. The Project

As argued by Kierans (1985), the case for the GRAND Canal rests on the recognition of four major water quantity issues. These are

(a) A shortage of water on the Canadian prairies

(b) Fluctuations in water levels and impending water shortages in the Great Lakes-St. Lawrence basin.

(c) Impending shortages of water for agricultural, industrial and urban use in the United States, especially the mid- and south-west.

(d) The need to avoid diversions of northward flowing rivers so as not to foreclose options for northern development.

According to Kierans, these problems would all be mitigated by the GRAND canal scheme. Very large volumes of water could be delivered to the Great Lakes for transmission to the Canadian West and the American mid-west and south-west, thus alleviating problems (a) and (c). Because the inflow and outflow of water from Lakes Michigan and Huron would be controlled, the level of these lakes could be stabilized, thus addressing problem (b). Finally, since none of the rivers flowing into James Bay would be diverted before it reached the ocean, problem (d) would be solved.

Kierans claims that the scheme will promote large increases in North American agricultural and industrial production. He claims support from the experience of recycling of freshwater from the IJselmeer in Holland and from the delta of the Sacramento River in California. Both projects are alleged to have generated very large benefits. Canada would capture some part of the benefits accruing to the United States through payments made by American authorities for the exported water.

Kierans also claims that the scheme would have many additional benefits. Among these are the stabilization of the James Bay shoreline, the creation of employment, the provision of a new network of electric power generating stations, and improved trade between Canada and the United States.

Opposition to the proposal has taken many forms. It is argued that water shortages in the United States and Canada can be alleviated through demand management (i.e. a reduction in the demand for water through conservation and diversion from lower valued uses) backed by rational water pricing. Alternatively, water exports are opposed on the grounds that the water will be required in Canada in the future. A water export scheme is seen as irreversible for all intents and purposes. Many environmental costs are to be expected from the construction and operation of such a project. These include possible changes in climate, biological damage through the transfer of harmful organisms across watersheds, and destruction of the recreational potential of some river valleys. Finally, social costs may be imposed on native peoples and others who could be displaced from traditional pursuits or whose communities could be disrupted by the booms and busts characteristic of resource development.

In the next section we examine the potential costs and benefits of the GRAND Canal project in more detail. To do so we must consider a specific variant of the proposal, while recognizing that the outcome of our analysis might be altered if a different variant were chosen. Indeed one of the virtues claimed for cost-benefit analysis is that it encourages optimization of proposals during the process of evaluation.

The proponents of the GRAND Canal have not committed themselves to any specific form of the project. Kierans (1985) simply states that eventually up to 20% of the natural runoff into James Bay would be made available for recycling and that the cost of facilities to impound James Bay water and deliver it to the Great Lakes would be of the order of $50 billion. No specific volume of water is mentioned. Informal calculations by other engineers suggest that the cost of such a system would be substantially higher, perhaps of the order of $130 billion (before allowance for interest during construction).

Basing our discussion on such informal calculations, we assume a maximum total diversion of 100,000 cfs (708 m^3/s) from James Bay with delivery (after evaporation losses) of 75,000 cfs to Georgian Bay. This water would be available to compensate for firm withdrawals from Lakes Superior, Michigan or Erie (see DeCooke, Bulkley and Wright (1984) for a discussion of possible routes) and for augmentation of natural flows to Lake Michigan-Huron in dry years. In the latter case provision must be made for discharge of larger than normal volumes during wet years. The south-western United States and western Canada thus obtain water in two forms: a guaranteed flow and an interruptible flow whose mean value depends on the variance of natural discharges into the Great Lakes. Presumably guaranteed flows would have a higher value to the receiving regions but would reduce benefits from water level stabilization on the Great Lakes.

The GRAND Canal scheme is only one of several large scale water diversion schemes which have been proposed in the past. Others include the North American Water and Power Alliance (NAWAPA) and the Central North American Water Project (CeNAWP) to divert waters from as far north as the MacKenzie river to the United States via the Rocky Mountain Trench and the Canadian Prairies respectively. (See Scott (1985, 29ff.) for discussion). Any serious evaluation of the GRAND Canal scheme would have to compare all three possibilities, as well as other ways of meeting water shortages, to a benchmark alternative. The benchmark adopted in this paper is continued reliance on natural drainage to the Great Lakes and no further diversions from them.

3. Costs

Table 1 sets out the main categories of costs and benefits associated with the GRAND Canal scheme and provides very rough estimates of some of them. The most important categories are capital cost of the project itself, the annual operating costs, the opportunity cost of the water, and finally environmental and social costs incurred during construction or operation of the project. The following paragraphs consider each category in more detail.

Capital and Operating Costs

Total capital costs are heavily influenced by the cost of constructing a dam across some fraction of James Bay. The remaining major item is the cost of construction of pumping stations: this cost varies with the designed capacity of the project. Table 2 reports a range of estimates of the total capital and operating cost. Case 3 represents Kierans's (1985) estimate of $50 billion. Cases 1 and 2 are drawn from informal engineering calculations. Case 1 considers a diversion of 2832 m^3/s (100,000 cfs) representing somewhat less than 25% of the estimated total run-off to James Bay. The volume of water transmitted is comparable to Case 3. Case 2 considers "recycling" virtually all the run-off from James Bay. Since the cost of the containing structure is the same in both examples, the estimated average cost falls sharply in the larger project.

To the direct cost has been added interest during the 15 years of construction. The conclusions hold for a wide range of interest rates. Interest during construction was calculated on the assumption that costs are evenly spread over the construction period. If costs are in fact more heavily concentrated at the end of construction, interest costs would be lower. A social discount rate of 8% has been adopted for the analysis presented here.

The total capital cost has been expressed as a lump sum as of the date of completion and as the equivalent annual payment required to amortize this sum over the hypothesized 80 year life of the work.

Annual operating and maintenance costs are dominated by the energy cost of pumping the water. This energy should be evaluated at its true social opportunity cost, namely the higher of its full cost of production (if it is produced by dedicated power generating stations) or the foregone revenue and consumers surplus from displaced consumption by domestic consumers and export customers.

Unquantified Costs

A number of costs have not been quantified in Table 1. Among these are the opportunity cost of the water exported and environmental costs incurred during construction and operation of the project. Information is not readily available about these costs, but some of them may be large.

The water that would be committed for export under the GRAND Canal scheme has alternative uses. In particular, it could be left to drain to James Bay as it normally does or it could be diverted to other final destinations, including the Canadian prairies. The value it would have in these uses is its opportunity cost.

If one excludes the social and environmental costs discussed below, the opportunity cost of the GRAND Canal water is probably low. The willingness of western Canada to pay for additional water supplies will not be significantly greater than the willingness of the South-west United States, and significant costs would be incurred in delivering the water from the Great Lakes to them. Nevertheless, should the GRAND Canal preempt the sale and delivery of James Bay water to Western Canada, the foregone revenues should be included as a cost of the project.

More significant are the environmental and social costs which might be caused by undertaking the project. Environmental effects of the project would include modification of the ecology of the James Bay coast and possible climatic changes due to the earlier freezing of the Bay. Unless new canals were built for the entire route to Georgian Bay, natural water courses would be submerged and subject to flooding. Some of these, for example the French and Mattawa Rivers, have high historic and recreational values. Moreover, many people place high value on the mere existence of water in its undisturbed natural state (Muller, 1985). The strong negative public reaction to the GRAND canal scheme indicates that the willingness to pay to avoid the scheme might be high. No cost-benefit analysis of the project would be complete without an attempt to gauge the magnitude of these costs.

Another set of costs should also be considered. Large construction projects generate considerable employment, but much of it is temporary. The boom and bust cycle generates social costs if migration of labour leads to high expenditures on housing and other social infrastructures which must later be abandoned. It may also disrupt the social structure of small northern communities. Full compensation for these losses should be accounted a cost of the project. Because relatively few people are involved, however, the total cost of compensation may not be very large.

In Table 1, no entry has been made for the opportunity cost of water, nor for the social and environmental costs of construction and operation. Some evaluation of these costs would be required before the GRAND Canal project could ever be allowed to proceed.

3. Benefits

As shown in Table 1, the main benefits claimed for the GRAND Canal can be grouped into the benefits of increased consumption of water, benefits from stabilization of water levels on the Great Lakes, the generation of power, and the provision of employment. Before considering them individually, some general comments on the measurement of benefits will be useful.

Economic Impacts versus Economic Benefits

Proponents of the GRAND Canal sometimes argue that one should not take a "user pay" approach to evaluating the benefits of the project, but should rather assume that only a small fraction of the total benefits of a water project are captured by the end user. As an example they cite studies such as Milliken's (1979) evaluation of the economic impact of the California Central Valley irrigation scheme and the study by Kulshreshtha and others (1985) of the impacts of irrigation projects in Alberta and Canada generally. The latter study, for example, claimed that only 15% of the total benefits of irrigation projects in Alberta accrue to the water users while 66% accrue to other Albertans and 19% to the rest of Canada. If the same ratio applied to benefits of water distributed from the Great Lakes, the total willingness to pay for water in the South-western United States would range up to $666 Canadian per thousand cubic metres[2], a figure comparable in magnitude to the total cost of delivering such water.

Such an argument is fundamentally wrong because it confuses economic impacts with economic benefits. The Kulshreshtha paper, for example, uses the terms interchangeably. It calculates the economic impact of irrigation by comparing the predicted level of gross domestic product (GDP) for Alberta in a world with and without the presence of irrigated agriculture using the techniques of input-output analysis.

The economic impact of an activity is legitimately measured by this technique. By the impact of an activity is meant the change induced in selected economic indicators (such as GDP, employment, or public revenues) as a result of the activity. It is assumed that if the activity were not undertaken, nothing would take its place. Thus, for example, Kulshreshtha et.al. have apparently compared the output of the Alberta economy with irrigated agriculture with an economy in which the net output of irrigated produce is zero but the net output of all other industries is the same as before.[3]

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[2] 100/.15 = 666

The economic impact may be divided into direct, indirect and induced effects. The direct effect is the change in output of the irrigated agriculture. The indirect effects are the increased levels of intermediate production required to support that output. One can also calculate an induced effect, caused by allowing the final consumption of other goods and services to expand as the economy grows. These impacts induced effects are often called multiplier effects.

The economic benefit of an activity is the gain realized by undertaking it. We say that a project is worth undertaking when its benefits exceed its costs. Accordingly benefits should be measured by the amount people would be willing to pay to obtain them. The economic impact of a project is not a good measure of what people would be willing to pay for the project for two reasons.

First, in calculating the impact of an activity such as irrigation, one implicitly assumes that the land, labour, capital and materials used have no alternative use. This is patently false. Even in an underemployed economy, many of the resources released from a declining industry find employment elsewhere. Thus, for example, the benefit received by labour from irrigation in Alberta is not measured by wages received in irrigation, but by the excess of wages received in irrigated agriculture over the amount that would have been received elsewhere. The economic impact of an activity overstates the benefits received from it to the extent that there are alternative uses for the resources employed in the activity.

Second, in calculating the impacts of a project, one frequently uses a "closed" input-output model to calculate induced effects. This procedure is equivalent to using the Keynsian multiplier discussed in elementary Economics texts. Problems arise because, as most economists now agree, the Keynsian multiplier is at best a short run phenomenon. In the longer run, the multiplier is reduced as other economic activities are crowded out by higher prices and interest rates. Rather than the multipliers of 1.7 and higher implied by input-output models, most large-scale econometric models of the Canadian economy show multipliers that decline from slightly over one in the first year of an activity to close to zero after ten years. This implies that the long run impact on GNP of any sustained government expenditure is close to zero. Thus the multipliers used in many economic impact analyses greatly overstate the true increase in GNP associated with an activity or project.

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[3] Alternatively, they may have increased the output of dryland agriculture by the estimated value of dryland crops which could be grown on the lands that are presently irrigated. The essence of the following argument is unchanged.

To summarize, the benefits of the GRAND Canal project cannot be measured by economic impact analysis, but only by the willingness of recipients to pay for more water. As we shall see, this willingness to pay appears to be low. We now consider individually each of the benefits claimed for the GRAND Canal.

Revenue from Water Exports

The benefits to Canada from exporting water beyond the Great Lakes Basin would be realized in the form of payments negotiated with various agencies in the United States. Since the United States will attempt to gain some net benefit from the water deal, these payments cannot exceed the total willingness of the United States to pay for additional water at the Great Lakes. The correct way to calculate a maximum willingness to pay (WTP) for water delivered to the Great Lakes is to estimate the willingness of end users to pay for additional water and then to deduct additional costs incurred in transporting the water beyond the Great Lakes. The result may overestimate total WTP if water from other sources can be delivered more cheaply.

Most evidence indicates that most end users of water are not willing to pay very much for additional volumes. Muller (1985) summarized estimates of the WTP for water in Canada for a number of uses. One must be careful in interpreting such data, since the methods and concepts underlying the various estimates may not be comparable. Nevertheless, irrigation uses were valued in the range of $19 to $36 Canadian per thousand cubic metres (at 1984 prices). U.S. studies cited by Veeman (1985, 57) implied values in the south-western United States as high as $69 Canadian per thousand cubic metres. Willingness to pay for water in industrial uses ranged from $19 to $124 Canadian per thousand cubic metres. Only municipal use had a potential value well above these figures. These figures must be viewed as highly tentative, since most are based on updating cost data from quite old studies.

The total cost of delivering water from the Great Lakes to the US South-west is estimated to be about 10 times greater than these WTP values. For example, DeCooke, Bulkley and Wright (1984, 14) estimate an average cost of $577 per acre foot (about $710 per thousand cubic metres - date and currency unspecified) to deliver water from the Great Lakes to the Ogallala reservoir. Clearly neither irrigators nor any other class of user in the US South-West (with the possible exception of municipalities) could afford to pay a positive price for water at the Great Lakes.

Consequently, the only reasonable market for GRAND Canal water lies with users closer to the Great Lakes[4]. These might be prepared to pay amounts up to about $50 or $100 per thousand cubic metres. The key question is then what quantity of water might conceivably be demanded at that price, since these regions are not affected by drought to the extent suffered by the South-west.

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[4] But see Scott (1985) who suggests that if the US government were prepared to pay the exorbitant cost of delivering water to the South-west, it might be willing to pay as much as 100 C$/Ml for make-up water.

Nevertheless, the demand for water in the Great Lakes region is expected to grow. Bruce (1984) suggests an annual growth in consumption of 2.7% per year to 2036. Such a growth rate implies a quadrupling of consumption in 52 years.

Experience with forecasting energy demands suggests that such high growth rates are unlikely to be realized. The IJC considers that projections beyond the year 2000 are too uncertain to use as a basis for planning and policy decisions (1985,31). Table 3 shows that the IJC's own most likely projection is that the rate of water consumption in the Great Lakes Basin will increase to between 161 cubic feet per second (cfs) and 238 cfs. If the willingness-to-pay were $50 per thousand cubic metres and if the increment, 79 cfs, were supplied entirely from James Bay water the total benefits would amount to about $124 million per year. If the consumption increase were twice that predicted by the IJC and if willingness-to-pay were $150 per thousand cubic metres, the total benefits would be $747 million per year. These are the low and high values reported in Table 1.

Stabilization of Water Levels

The second major benefit claimed by proponents of the GRAND Canal is stabilization of the water levels of Lakes Michigan and Huron. Proponents have not cited any studies indicating the order of magnitude of these benefits but at first glance they appear to be low.

Stabilization of Lakes Michigan and Huron would entail using the GRAND Canal to augment natural inflows during times of drought and discharging extra large volumes of water through the various diversions in times of high water. This implies that, in dry seasons, not all the capacity of the GRAND Canal would be available for export beyond the Great Lakes basin. Furthermore, discharge of excess water through the Mississippi River system could cause flood damages and would require preventive engineering works. In short, stabilization of lake levels would seem to imply both an increased variance of water deliveries beyond the Great Lakes and increased costs to water importers. Thus it appears that there would be a trade-off between water export benefits and water level stabilization benefits.

Some idea of the order of magnitude of water stabilization benefits can be obtained from the International Joint Commission's (1983) report on limited regulation of Lake Erie. This report summarizes studies undertaken to determine whether limited regulation of Lake Erie would be in the public interest. Three schemes to increase maximum outflows from Lake Erie were considered. Capacities ranged from 100 to 710 m^3/s. The maximum reduction in maximum Lake Erie levels would be 32 cm and the maximum reduction in range would be 25 cm.

For the largest plan, there would be gains of up to $59 million per year (at 1979 prices and deliberately unspecified currency) in reduced flood damages and gains of up to $68 million per year in improved beach recreation. There would be losses of up to $115 million per year in increased navigation costs due to lower water levels in shipping channels, losses of up to $24 million per year in reduced power production caused by less efficient use of available water, and losses of up to $35 million to US recreational boating.

It appears, therefore, that the chief benefits to be expected from stabilization of water levels would be first, reduced flood damages and improved recreational opportunities from beaches which are no longer flooded in high water seasons and secondly improved access to recreational boating during dry seasons. Water stabilization would also imply environmental costs, particularly by reducing the intermittent flooding of wetlands.

The IJC study clearly indicates that the benefits of water level stabilization on Lake Erie would be modest. If we take only the positive benefits and adjust to 1985 price levels, we obtain an annual benefit of about $156 million per year. It is not clear how to apply this to Lakes Michigan and Huron which have more shoreline but lower density development. If we double the amount, we still obtain an estimated benefit of only 0.3 billion dollars per year. This is the high estimate reported in Table 1. We take zero as the low estimate.

Power Benefits

A further benefit claimed for the GRAND canal is the generation of hydroelectric power. It should be clear that laws of physics ensure that the scheme will be a net consumer of energy - more energy is required to lift the water to the arctic watershed than can possibly be extracted on the descent. Furthermore, some water will be lost to evaporation on the journey, and hence unavailable for the generation of power. At best we can hope that the power generated in descending will partially offset the power required to lift.

To obtain a rough estimate of the cost savings, suppose that from 50% to 70% of lifting energy can be recovered in downstream generation at a cost of $5.70 per thousand kilowatt-hours. This was the average financial cost of hydraulic power in Ontario, 1984, excluding water rentals. (Ontario Hydro, 1984). Assuming a total pumping energy requirement of 48.9 billion kilowatt-hours per year, the annual cost saving would lie between 0.8 and 1.1 billion dollars, as shown in Table 1.

Since the benefits from hydro generation only partially offset the pumping costs, it would be reasonable to use them to reduce the estimated net cost of the project and to exclude them from the benefit side of the ledger. The present procedure has been adopted purely for expositional reasons.

Employment Benefits

A final category of benefit claimed for the GRAND Canal is the creation of employment. This claim is dubious, since there are two strong arguments for not giving any employment credit to such a program.

First, most economists agree that unemployment levels are determined in the short run primarily by the level of aggregate demand (as influenced by fiscal and monetary policies adopted by the Federal government) and in the long run by the underlying characteristics of the economy which generate the "natural rate of unemployment". The government may deliberately choose not to reduce aggregate unemployment for fear of stimulating inflation or causing an excessive depreciation of the exchange rate. Under these circumstances it is inconsistent to credit a water project for employment creation while holding back employment creation in the rest of the economy.[5]

Secondly, any large expenditure of money will cause an short run increase in the level of employment. It is inconsistent to credit a project with creating employment without at the same time debiting it for the employment which was lost by not spending funds elsewhere.

These considerations suggest that no project should be given credit for employment creation unless the jobs are created in areas or occupations which have been explicitly designated as targets for government employment creation. Even under these circumstances, one must be very careful not to overestimate the employment created and not to give excessive credit for it.

The employment directly created by a project can often be calculated from estimated labour costs and average wage rates. To this is often added the secondary employment generated by the multiplier effect discussed above. As noted then, multipliers derived from input-output models tend to overstate the multipliers derived from macroeconometric models which incorporate the macroeconomic feedbacks which tend to stabilize the economy. Consequently, the secondary employment effects of a project will be overstated through their use.

Moreover, much of the labour which would be drawn to a project such as the GRAND Canal is not completely unemployed. Only the wages in excess of its current compensation can conceivably be counted as benefits, and even here allowance must be made for premiums such as isolation pay. It might be argued that by employing previously unemployed labour the government reduces its payments of unemployment insurance, but these payments in part reflect whatever utility the unemployed worker derives from his (involuntary) leisure and, in any case, recent work in economics has emphasized that large construction projects may draw workers into a pool of temporary employees who will claim unemployment insurance when they are laid off.

Such arguments suggest that it would be unwise to credit the GRAND Canal with large employment generation benefits. As a rough indicator, one could take an arbitrary fraction of the wage bill to estimate them. We must also make an assumption about the share of labour costs in the total project. In Table 1 it has been assumed that between 5% and 10% of total capital plus operating costs of the project are available as employment benefits. This yields a range of from $0.2 to $2.2 billion per year annualized over the 80 years of the project's life.

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[5] A project as large as the GRAND Canal might cause additional problems for stabilization policy by creating inflationary bottlenecks in key industries.

5. Discussion

Reviewing the estimates presented in Table 1, we note that the present value of the quantified benefits from the GRAND Canal scheme ranges between $16.1 billion and $46.3 billion. These benefits are equivalent to an annual flow of between $1.3 and $3.7 billion over the 80 year life of the project. The present value of capital and operating costs is estimated to lie between $121.7 billion and $276.4 billion. Annualized costs lie between $9.8 and $22.2 billion. Possibly important costs remain unquantified. These include the opportunity cost of exported water and the social and environmental costs incurred during construction and operation of the scheme. Thus the quantified costs exceed the benefits by a factor of 6 or 8.

The largest benefits, from power and employment, arise in effect from correcting the price of certain inputs (energy and labour) in calculating net costs. They were treated as benefits largely for expositional purposes. In computing a benefit/cost ratio they might better be viewed as negative costs than as positive benefits. If we take this view than the GRAND Canal project has a benefit-cost ratio in the neighbourhood of 0.07 to 0.15.

These estimates were developed in order to gauge the economic feasibility of the GRAND Canal project and to identify the areas in which further information is most urgently needed. The estimates suggest that the GRAND Canal project is not economically viable. Net Benefits are consistently negative. This conclusion is not dependent upon the particular rate of interest chosen. In computations not reported at length, net benefits were estimated to lie between -93 and -178 billion dollars at a discount rate of 5%, and between -117 and -262 billion at a discount rate of 10%.

This conclusion arises from the limited benefits which flow from the project. Estimated benefits were small for four reasons. First, both the estimated willingness to pay for exported water and the potential volume of exported water were low. Secondly, the losses from flooding and low water on the Great Lakes were estimated to be two orders of magnitude smaller than the estimated costs of GRAND Canal water. Thirdly, care was taken not to confound the economic impact of the project with economic benefits. Finally, only a limited credit was allowed to the project for employment creation.

If further study of this project is undertaken, the most pressing need is to identify a realistic market for the large volumes of water contemplated. Without such a market, additional discussion seems pointless. If, at prices in the order of $100 to $200 per thousand cubic metres, a market for up to 67 billion cubic metres of water per year can be found, then high priority should be placed on refined estimates of the engineering cost of the project. To be taken seriously, the proponents must demonstrate that it might be possible to deliver a specified flow of water to the Great Lakes for combined capital and operating cost in the area of 100 $C/Ml. This is one third the cost estimated in Case 1 of section 3.

Much has been made of the social and environmental costs of a GRAND Canal project. Without much more solid evidence of the financial viability of the scheme, it seems premature to attempt to evaluate these costs with reference to this specific project. Much too little is known, however, about the intrinsic and recreational value of natural waterways and wetlands. A systematic study of these would provide valuable information for the evaluation of other major resource projects as well as studies of the effects of acid precipitation and climatic change.

6. Conclusion

This paper has used a cost-benefit framework to organize a discussion of the economics of the GRAND Canal project. The estimated costs and benefits are very crude. Nevertheless, the exercise has been useful in judging the feasibility of the project and in identifying issues of critical importance.

On the basis of available information, the GRAND Canal scheme seems to be quite unviable. Estimated net benefits are a small fraction of estimated costs, even before quantification of social and environmental costs and the opportunity cost of the water itself. To reverse this assessment would require clear identification of a large potential market for exported water and a well specified engineering plan to deliver the water at costs below those now contemplated.

The cost-benefit framework has proven useful in organizing our discussion and in emphasizing the importance of realistic estimates of potential markets. The techniques developed by cost-benefit analysts have helped in avoiding the misuse of economic impact assessment and in avoiding excessive emphasis on the employment creation aspect of the scheme.

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TABLE 1

SUMMARY OF COSTS AND BENEFITS OF THE GRAND CANAL SCHEME
(in billions of 1986 dollars)

	Annualized		Present Value	
	Low	High	Low	High
BENEFITS				
Quantified				
Consumption Uses	0.1	0.7	1.6	9.3
Stabilization of Great Lakes	0	0.1	0.0	1.2
Power	0.8	1.1	10.0	13.7
Employment	0.5	2.2	6.1	27.6
Total Quantified Benefits	1.4	4.2	17.6	51.9
COSTS				
Quantified				
Capital	7.3	19.1	90.5	237.8
Operating and Maintenance	2.5	3.1	31.2	38.6
Total Quantified Costs	9.8	22.2	121.7	276.4
NET QUANTIFIED BENEFITS	-8.3	-18.0	-104.1	-224.5
NET BENEFIT-COST RATIO				
Net Benefits	0.6	3.1	7.6	38.2
Net Costs	9.0	21.1	111.7	262.7
Benefit-Cost Ratio	0.07	0.15	0.07	0.15
UNQUANTIFIED COSTS				
Opportunity Cost of Water				
Environmental				
Social				
ASSUMPTIONS				
Real Discount Rate	8.0%			
Assumed Lifetime of Project	80 years			
Assumed Construction Period (years	15			

NOTE

Power Benefits have been subtracted from both total benefits and total costs before computing the benefit-cost ratio.

TABLE 2

ESTIMATED CAPITAL AND OPERATING COSTS FOR GRAND CANAL PROJECT

Line	Item	Case 1	Case 2	Case 3
1	Water Diverted (m3/s)	2832	11327	2832
2	Evaporation Losses (percent)	25%	25%	25%
3	Water Delivered to Great Lakes (m3/s	2124	8495.25	2124
4	Water Delivered (Tl/a)	67.0	267.9	67.0
5	Direct Costs			
6	James Bay Containing Dam (G$)	70.0	70.0	
7	Pumping Stations (G$)	14.0	55.6	
8	Conveyance Canal			
9	James Bay to Amos	7.0	10.7	
10	From Amos to Great Lakes	9.1	12.7	
11	Contingency (25% of 6..10)	25.0	37.3	
12	Engineering and Management			
13	5% of 6..11	6.3	9.3	
14	Total Direct Costs	131.4	195.8	50.0
15				
16	Real Discount Rate	8.0%	8.0%	8.0%
17	Construction Period (years)	15.0	15.0	15.0
18	Interest During Construction	106.4	158.6	40.5
19	Future Value of Direct Costs	237.8	354.5	90.5
20				
21	Assumed Life for Amortization	80.0	80.0	80.0
22	Annualized Capital Costs (G$/a)	19.1	28.4	7.3
23				
24	ANNUAL COSTS			
25	Pumping Energy (TWh/yr)	81.5	325.8	81.5
26	Cost per MWh	25.0	25.0	25.0
27	Total Energy Cost (G$)	2.0	8.1	2.0
28	Annual O&M (5% of 22+27)	1.1	1.8	0.5
29				
30	Total Annual Costs	3.1	10.0	2.5
31				
32	TOTAL ANNUALIZED COSTS			
33	in billion $	22.2	38.4	9.8
34	in $/Ml	330.8	143.3	145.7

Case 1: Transmission of roughly 25% of inflow to James Bay
Case 2: Transmission of most of inflow to James Bay
Case 3: Transmission of roughly 20% of inflow to James Bay: Kierans's Capital Cost estimate.

UNITS
Ml Megalitre = 1000 cubic metres
Tl Teralitre = 1 billion cubic metres = 1 cubic km
TWh TeraWatt.hour = 1 billion kWh
G$/a = billion $ per year

SOURCE
Cases 1 and 2: Informal Engineering estimates
Case 3: Elaboration of Kierans (1985) estimate of Capital Cost.

TABLE 3

ESTIMATED CONSUMPTION BENEFITS FOR GRAND CANAL PROJECT

ITEM	LOW	HIGH	NOTE
1 Consumption in year 2000 Great Lakes Basin (cms)	161	238	a
2 Consumption in year 1975 Great Lakes Basin (cms)	82	159	b
3 Predicted Increase, 1975-2000 (cms)	79	79	c
(Gl/a)	2488.5	2488.5	
4 Assumed Consumption met from James Bay water (Gl/a)	2488.5	4977	
4 Willingness to Pay ($/Ml)	50	150	
(M$/Gl)	0.05	0.15	
5 Total Willingness to Pay (M$/a)	124	747	

NOTES

a IJC (1985, 36)
b IJC (1985, 30)
c 1 cms = 31.5 million cubic metres/annum = 31.5 Gl/a

UNITS

cms cubic metres per second
Ml Megalitre = 1000 cubic metres
Gl Gigalitre = 1 million cubic metres = .001 cubic km
M$/a = million $ per year

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